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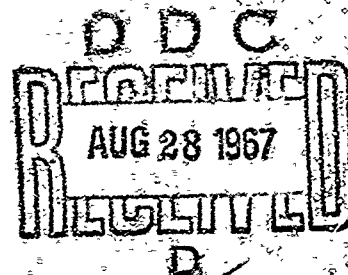
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**CARBON DIOXIDE ABSORPTION AND
DESORPTION BY TRIS WITH CARBONIC
ANHYDRASE**

JOHN P. ALLEN

TECHNICAL REPORT AFEDL-TR-67-69

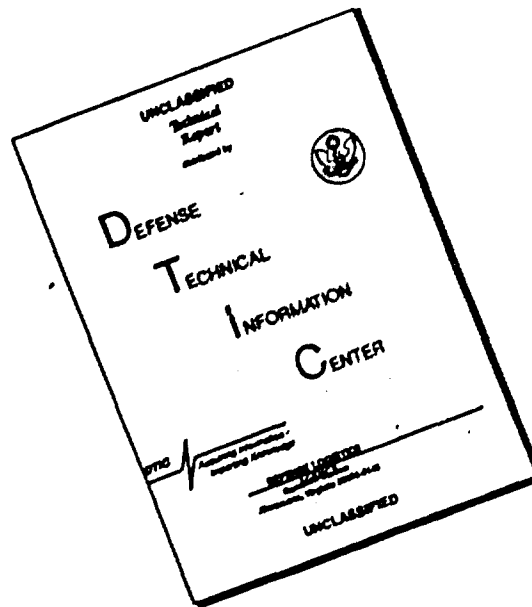
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FOREWORD

This report was prepared by the Air Force Flight Dynamics Laboratory (AFFDL), Directorate of Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The work was initiated under Project No. 6146, "Atmosphere and Thermal Control," Task No. 614611, "Biochemical Techniques of Carbon Dioxide Fixation," Dr. John P. Allen (FDFE), Project Engineer.

This report summarizes the investigations and results of work performed in the atmosphere regeneration and control laboratories of AFFDL from January 1966 to October 1966, emphasizing studies on carbon dioxide absorption and desorption by a tris buffer solution containing the enzyme, carbonic anhydrase. The manuscript was released by the author in December 1966 for publication as a technical report.

All of the items compared in this report were commercial items that were not developed or manufactured to meet Government specifications, to withstand the tests to which they were subjected, or to operate as applied during this study. Any failure to meet the objectives of this study is no reflection on any of the commercial items discussed herein or on any manufacturer.

This technical report has been reviewed and is approved.


WILLIAM C. SAVAGE
Chief, Environmental Control Branch
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ABSTRACT

One concept of carbon dioxide control in aerospace vehicle atmosphere regeneration and control requires an efficient gas absorber which is effective in a moist gas stream. A tris (tri(hydroxymethyl)aminomethane) solution containing the enzyme, carbonic anhydrase (CA), was studied as to carbon dioxide absorption and desorption. The carbon dioxide content and the pH changes were monitored during the recycling of a gas mixture through the absorber solution. Desorption was accomplished by nitrogen aeration. The application of DC potentials to the absorber solution indicated an acceleration of carbon dioxide desorption. Vacuum desorption of carbon dioxide without nitrogen bubbling was not effective. Nitrogen aeration at 33°C was more effective than at room temperature or at 13°C. The pH of the enzyme-tris solution varied inversely with the carbon dioxide content. The tris solution was a more effective carbon dioxide absorber than 0.1 N NaOH when the enzyme was present. A long time stability of approximately five weeks for a 70-ml aliquot of tris at 0.1 N with 10 mg of CA was indicated by the repeated absorption and desorption runs made in the regeneration studies. The application of a buffered enzyme solution to carbon dioxide control is supported by a rapid removal rate from a recycling air stream and a regeneration capability. This concept of carbon dioxide control requires additional research for the evaluation of techniques to accelerate the carbon dioxide desorption process.

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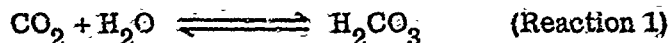
SECTION I

INTRODUCTION

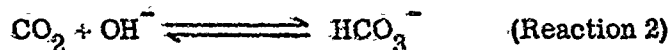
This report discusses research on carbon dioxide absorption and desorption by a tris solution containing carbonic anhydrase (CA). Previous studies in the Air Force Flight Dynamics Laboratory (References 1 and 2) and those of Graf (References 3 and 4) supported this concept of a CA catalyzed tris solution for carbon dioxide control. Park (Reference 5) proposed the use of the enzyme for carbon dioxide control in submarine atmosphere control systems but presented little supporting data. The experimental work reported here included a verification of the carbon dioxide absorption and desorption by a tris solution with CA, and a comparison of this sorption process with that of standard carbon dioxide absorbers. The regeneration of the carbon dioxide absorption capacity of the enzyme-tris solution was investigated by use of nitrogen aeration under a change of temperature, pressure, and pH. The methods used were arbitrarily standardized so that day-to-day absorption and desorption curves could be compared. The results are presented in the form of carbon dioxide absorption curves which indicate significant carbon dioxide concentration changes and pH change curves. Tabulated data compares the removal rates as percentages, and the capacity and effectiveness in relation to standard absorbers. The information is discussed with the aim of applying this enzymic catalysis of carbon dioxide hydration to the atmosphere control problem in manned environmental control systems.

This effort provides further information on the stability, capacity, and regenerability of an enzymic carbon dioxide absorber as a liquid system, with no direct consideration given for operation in a zero gravity environment. It has been suggested that liquid gas absorbers would find application in induced gravity environments in rotating devices. However, the approach to further work with enzymic absorbers would be in the use of buffered enzyme systems stabilized on inert substrates. These could be functional in a highly humid atmosphere such as would be present in an atmosphere control system after the air has been cooled to its dew point for humidity control. The high humidity content favors the hydration concept for carbon dioxide control. The General American Transportation Corporation (GATC) concept using the "Gat-o-Sorb" material is referenced here in a NASA sponsored effort for a carbon dioxide absorber (Reference 6).

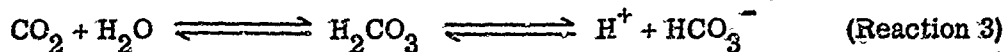
The theoretical basis for this work was the catalysis of the reaction of carbon dioxide with water such that at pH's less than 8, Reaction 1 occurred:



At pH's greater than 10, Reaction 2 occurred:



Between pH 8 and 10, both reactions occurred and the overall reaction was a normally rapid reversible inorganic hydration reaction, Reaction 3:



Enzyme activity in the pH range of 8 to 10 was high and evidence indicated that the enzyme catalyzed both reactions (Reference 7).

The absorption of carbon dioxide from air in tris solution involved (1) the solution of carbon dioxide in the solution, (2) hydration of the carbon dioxide in the formation of carbonic acid or the reaction of carbon dioxide with hydroxyl ions in the formation of a bicarbonate ion,

(3) the dissociation of the carbonic acid to hydrogen and bicarbonate ions, and (4) the reaction of the bicarbonate ions with the tris in the formation of a salt, a bicarbonate. The buffering action of tris removed the hydrogen ions formed in the dissociation of the carbonic acid and thus maintained the basic pH's favoring both the enzymic activity and the carbon dioxide reaction with hydroxyl ions. The sequence of reactions resulted in a state of equilibrium determined by the carbon dioxide concentration, temperature, and dissociation constants. CA catalyzed the attainment of this equilibrium. The apparent dissociation constant of carbonic acid increased directly with temperature as did the enzyme activity. The solubility of carbon dioxide in water decreased with temperature. Since the overall reaction was a reversible hydration, with an increase in temperature and CA present carbon dioxide desorption might be expected to accelerate provided the carbon dioxide would be vented from the solution. This desorption process was evaluated.

SECTION II

BACKGROUND INFORMATION

The control of carbon dioxide in air by use of a gas absorption tower using a liquid absorber is a proven and usable method. The experimental research areas concerning this method stress the use of new absorbers, new packing materials, gas flow dynamics, surface properties, chemical reactions in the sorption process, etc. The mechanics of the gas absorption in the liquid absorber have been extensively investigated (Reference 8). Carbon dioxide has been absorbed by alkaline solutions of sodium carbonate (References 9 and 10), potassium carbonate (Reference 11), and basic solutions of amines such as monoethanolamine (Reference 12), ethyl morpholine (Reference 13), and diethanolamine (Reference 13). These amine absorbers were regenerable in that the absorbed gas was released upon heating the absorber solution to boiling, thus requiring considerable power. Another technique was to regenerate with ambient air that had less carbon dioxide than the air being controlled, as with the carbonate absorbers.

The chemical absorbers essentially are reactants with carbon dioxide forming bicarbonates and carbonates in solution. The process of absorption was controlled by various gas flow factors, various absorption liquid characteristics, the gas-liquid interface properties, the chemical reactions occurring, and the physical parameters for the absorption tower. These are usually discussed in studies of gas absorption. Graf (Reference 4) discussed this gas absorption process as it applies to a tris solution absorber for carbon dioxide with CA. He used both a bubbling tower and a standard disc tower, and discussed absorption temperatures, wetting rates, gas flow rates, gas-liquid ratios, rates of absorption, overall coefficient on the gas phase basis, the log means driving force, the gas phase efficiency, and the flow pattern of the absorber. His conclusions were rather unique in that he recommended the use of tris for carbon dioxide removal, a compound that was recommended for use as a basic standard because it did not absorb carbon dioxide from the air when in crystalline form or as a solution (Reference 14).

A recycling air loop apparatus used in prior work (Reference 2) simulated a closed ecological system in that a total volume of gases was monitored during the carbon dioxide control process. The tris buffer demonstrated a carbon removal capability which was enhanced by the addition of CA. The absorber with the enzyme was effective in accelerating the carbon dioxide removal from the recycled air stream. However, the reverse process of desorption of carbon dioxide from the tris solutions was not adequately evaluated. The reaction was limited in part by the thermal inactivation of the enzyme and the effect of temperature on the dissociation constants in the overall hydration reaction of carbon dioxide.

The experimental work under this effort attempted to quantify the carbon dioxide desorption reaction factors such as temperature changes and nitrogen aeration in their effect on the regenerability of the enzyme-tris absorber in short time intervals of 30 to 60 minutes.

SECTION III

EXPERIMENTAL APPROACH

In this effort, the emphasis was placed on evaluation of possible techniques which would induce a rapid carbon dioxide desorption from an enzyme-tris solution after a carbon dioxide absorption run in an air loop apparatus using carbon dioxide at various concentrations. These concentrations were 270 ppm carbon dioxide in nitrogen, 0.4% in air, 4.92% in air, and 5.0% in nitrogen. The quantity of carbon dioxide in the air loop was based on a loop volume of 880 cc so that at 5.0%, there was 43.296 cc of carbon dioxide in the air loop at 25° and 740 mm Hg. For the other concentrations of gas used in the air loop the amount of carbon dioxide would be correspondingly less. The carbon dioxide was monitored by IR carbon dioxide analyzers while the g.v. were being recirculated through the air loop apparatus (Figure 1); the carbon dioxide concentration was recorded continuously during the absorption process and during recycling. The absorber solution was freed of dissolved carbon dioxide by nitrogen aeration before being valved into the air stream. The pH of the solution was monitored during the absorption process.

*All temperatures are degrees centigrade.

SECTION IV

APPARATUS AND MATERIALS

1. APPARATUS

The air loop apparatus used in previous carbon dioxide absorber studies (References 1 and 2) was modified for use in this work. The apparatus consisted essentially of an air recirculating pump, a CO₂ analyzer, and a sampling loop connected by 1/4 in. copper tubing with valving and flow control devices. The air loop apparatus used in this work is sketched in Figure 1 and consists of the following components:

1. Air Circulating Pump, DynaVac Pump, Model S
Cole-Parmer Instrument and Equipment Co.
2. Trap, Gas Purifier, Model 450
Matheson Co.
3. Flowmeters, Tube 2-65A (0-100%) and Tube 2-65B (0-5 cfm)
Brooks Rotameter Co.
4. Gages, 10-0-10 in. Water, Magnehelic, Differential Pressure
E. W. Dwyer, Inc.
5. Analyzer, IR, Carbon Dioxide 0-5% Model 15A
Beckman Instrument Co.
6. Analyzer, IR, Lira Model 200 CO₂ 0-300 ppm
Mine Safety Appliances Co.
7. Recorder, Multirange
E. H. Sargent & Co.
8. Valves, 2-Way, 3-Way, and 4-Way
Conant Brothers Co, Inc.
9. "U" Tube, Pyrex, With Indicating Drierite
10. Trap, Pyrex, Glass, Vapor, Vacuum Line, Cold Type, Internal
Volume 195 cc With 1/4 in. ID Polyurethane Connecting Tubing
11. Sampling Cell, "H" Shaped Cell, Lucite With Extra Coarse Gas
Dispersion Glass Plug, Internal Volume 190 cc, With 1/4 in. ID
Polyurethane Connecting Tubing
12. Midvale Bulbs, 4, Connected With Polyurethane Tubing
13. Bubbler Tube, With Trap, Internal Volume 190 cc, With 1/4 in. ID
Polyurethane Connecting Tubing

The apparatus differed from that of previous studies in that an "H" shaped sampling cell (Figure 2) was used. The loop volume was increased by moving the water vapor trap into the air loop instead of being used with the sample loop. The total volume for the loop and the

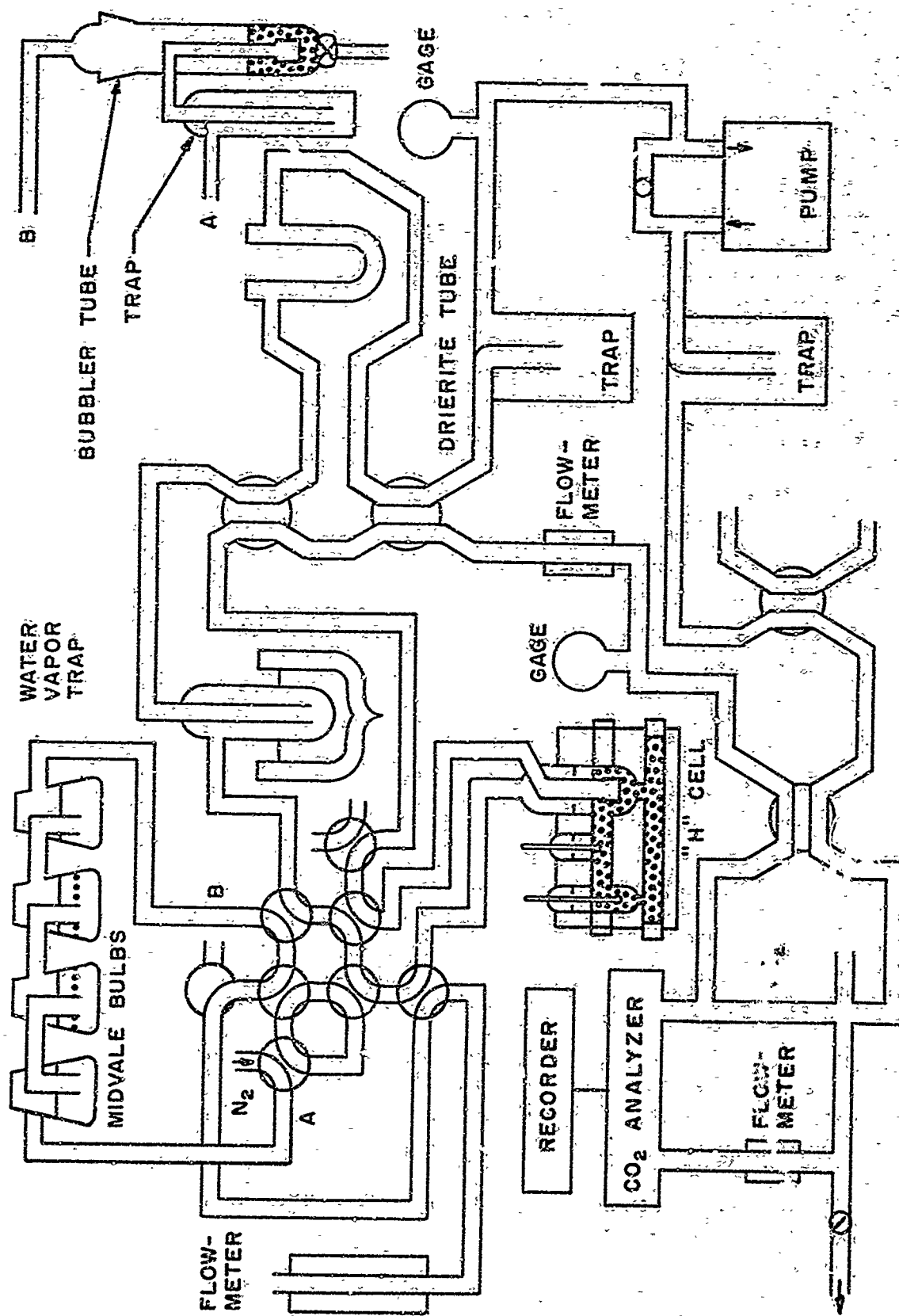


Figure 1. Air Loop Apparatus

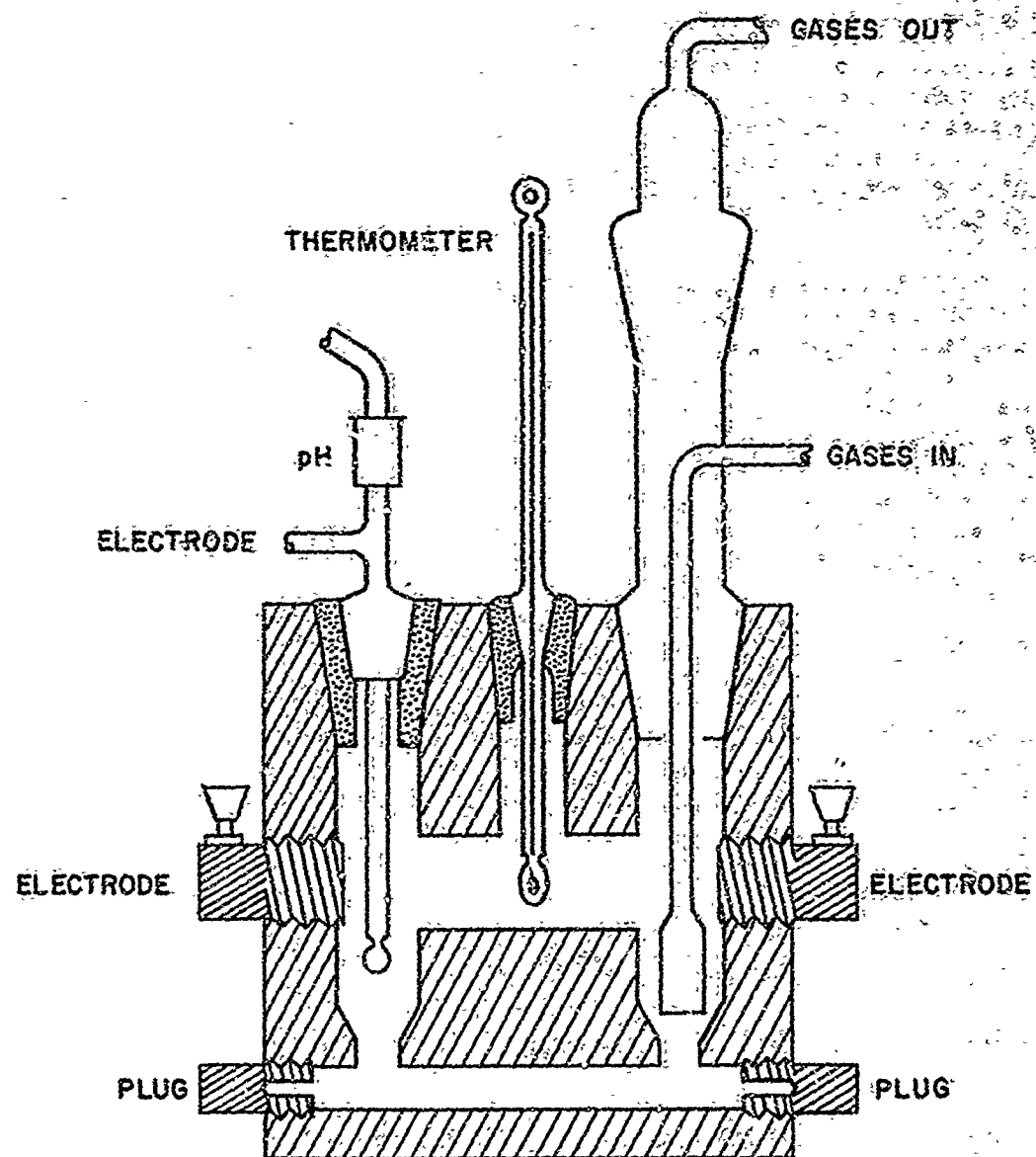


Figure 2. "H" Shaped Absorption Cell

sampling cell was calculated from carbon dioxide dilution curves at 25° and 740 mm Hg pressure. Valving allowed the use of four Midvale bulbs in a trap-trap-sample-trap series so that the absorption solution at 25 ml aliquots could be run in the air loop. In addition, a bubbler tube with an in. gas tube for a trap was used in a test comparison of NaOH, Ba(OH)₂ and tris solutions in 10, 20, or 25 ml aliquots as carbon dioxide absorbers. The bubbler tube was also used to trap carbon dioxide desorbed from the tris plus enzyme solutions by nitrogen recirculation and aeration at the three temperatures evaluated: 15°, 25°, and 33°. The bubbler tube was also used when a DC potential was applied to the electrodes on the "H" cell with the flow-through nitrogen aeration technique. The bubbler tube was connected to the air loop replacing the midvale bulbs.

The "H" cell was a gas absorption tube with provision for temperature sensing, heating or cooling, for pH sensing and measurement, for medium recirculation and for applying a DC potential across the medium. Figure 2 is a schematic of the "H" cell.

The volume of the "H" cell assembled and with the connecting tubing was 190 cc as measured with water at 18°. The "H" shape internal volume made use of the bubbling gases to initiate a circulation of the absorber solution with the gas bubbles into the horizontal portion in which the temperature was sensed. Further circulation of the solution into the other section of the cell allowed for pH sensing or for the heating and cooling by a cold finger condenser. The absorber solution was used in 70 ml aliquots and revealed satisfactory circulation in the cell.

2. MATERIALS

Significant in this investigation were the materials that provided comparisons of the carbon dioxide absorption by tris solutions of the enzyme with other standards. The compounds used were either CP or reagent grade chemicals. Solutions were made in distilled water. The gases used were 270 ppm carbon dioxide in nitrogen, 0.4% carbon dioxide in air, 4.92% carbon dioxide in air, and 5.0% carbon dioxide in nitrogen. The analyses were performed by Air Products and Chemicals, Inc., or by Matheson Co., the suppliers of the gas mixtures. The nitrogen gas was 99.5% water-pumped and was passed through a soda lime canister before use in aeration or as the zero gas in standardizing the analyzers.

The compounds used were as follows:

1. Tris (tri-hydroxymethyl)aminomethane, 99.94% 0.2 and 0.1 M Solutions
Eastman
2. Carbonic Anhydrase, 100 mg/10 ml of 0.05 M Tris Solution
Bionutritional
3. Sodium Carbonate, Reagent, 0.2 N Solution
4. Sodium Hydroxide, Standard Solution, 2.000 N Solution
Analytical Chemists of Cincinnati
5. Hydrochloric Acid, Standard Solution, 2.000 N Solution
Analytical Chemists of Cincinnati
6. Barium Hydroxide, Reagent, 0.2 N Solution
Matheson
7. Monoethanolamine (MEA) Tech, 0.1 M Solution
Matheson

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8. Potassium Chloride, Reagent, 0.1 N Solution
Matheson
9. 2-Amino-2-Methyl-1,3-Propanediol, 0.05 M Solution
Matheson
10. Tetramethyl Ammonium Chloride, 0.05 M Solution
Matheson
11. Sodium Bicarbonate Reagent, 0.2 N Solution
12. Neutral Red 0.01% in 50/50 Alcohol, pH 6.8-8.2
13. Potassium Hydroxide, 0.2 N Solution
Merck
14. Drierite, Indicating, Mesh 8
Hammond Drierite
15. Soda Lime 4-8 Mesh
Wills
16. Tris-Maleate Buffer, 0.2 M Solution

SECTION V

METHODS AND PROCEDURES

1. AIR LOOP ABSORPTION-DESORPTION

The air loop apparatus shown in Figure 1 and the "H" cell in Figure 2 were used to evaluate the carbon dioxide absorption by the various solutions in 70 ml aliquots. In this method, the air loop was first filled with the carbon dioxide-containing gas mixture which was either 270 ppm carbon dioxide in nitrogen, 0.4% carbon dioxide in air, 4.92% carbon dioxide in air, or 5.0% carbon dioxide in nitrogen by flushing with this gas mixture. The gas analyzer was standardized to read on the recorder 135 mm for the 270 ppm carbon dioxide in nitrogen, 80 mm for the 0.4% carbon dioxide in air, or 150 mm for the 5.0% carbon dioxide in nitrogen. The 4.92% carbon dioxide in air was indicated at 147.6 mm on the recorder. After calibration and standardization of the carbon dioxide analyzer and the recorder, the flushing gas was valved off and the air recirculating pump turned on. The gases in the air loop during the mixing were monitored as to carbon dioxide content. The flushing and recirculating of the gases in the air loop were repeated until the recirculating gases indicated a steady value of carbon dioxide on the recorder to correspond to the millimeter range noted above.

The "H" cell was connected in a sample loop but was separated from the sample loop by means of 4-way valves. In a carbon dioxide absorption run the sample cell was flushed with nitrogen which had passed through a canister of soda lime, to assure carbon dioxide free nitrogen. Nitrogen flushing was timed for 30 minutes for runs as a standardized condition for the air loop, the empty "H" cell, distilled water blanks, and a run using NaOH. However, when tris solution with or without the enzyme was being evaluated, the nitrogen period was at least one hour; the time of aeration depended upon the type of solution being evaluated and the prior testing of the absorber solution since one solution may have been used in a series of runs lasting several days.

Upon completion of the nitrogen aeration period for the "H" cell and its contents, the nitrogen stream was valved off and the recirculating air loop stream with the carbon dioxide-containing gas mixture was valved in. The change in carbon dioxide concentration was continuously recorded, the temperature read, and the pH monitored and recorded during the run until a steady carbon dioxide concentration was indicated on the recorder.

After a run with an absorbing solution in the "H" cell, the sample loop was valved off and the air pump turned off. The air loop was then flushed with the carbon dioxide-containing gas mixture and thus refilled with gases to attain a constant carbon dioxide content in the recirculating gas stream for another run.

2. SAMPLE LOOP PROCEDURE

In the sample loop, the procedure following the absorption run varied. By continued nitrogen aeration, the desorption of the absorbed carbon dioxide occurred with time and was evaluated by monitoring and recording the pH change. The temperature of the sample absorber solution was changed by recirculating water through the cold finger condenser which replaced the pH electrode in the "H" cell during either the heating or cooling mode of operation. For cooling the absorption solution, water at 2° was recirculated through the cold finger using a varistaltic pump; the temperature of the absorber solution was cooled to a 12° to 15° range. When 45° water was recirculated by the water bath recirculator through the cold finger condenser, the solution temperature changed to 33°; with 55° water, the solution temperature attained was 40°. These changes in solution temperature were slow and occurred gradually over a 30- to 60-minute interval. The pH of the absorber solution was not monitored during the heating or

cooling periods but was measured after a stable temperature was attained; the cold finger condenser was removed and the pH electrode inserted and the pH measured without temperature compensation to obtain an approximate pH value.

With the vacuum desorption method, a vacuum of 28 inches of mercury was applied to the open end of the flowmeter in the sample loop. The nitrogen gas had been valved off but was opened slightly to provide a bubbling gas for agitating the solution. The pH was not monitored when vacuum was applied to the "H" cell. Effects of temperatures at 15°, 25°, and 30° with vacuum were evaluated for carbon dioxide desorption with nitrogen bubbling for time periods of 30 and 60 minutes.

Quantitative data on the carbon dioxide desorbed was obtained in the following manner. After an absorption run with an absorber solution, the sample loop was valved off and kept closed, and the gas bubbler tube with the impinger flask was valved in with 10 ml of 0.2 N NaOH and used as a trap. The residual carbon dioxide in the air loop was removed by the recirculation of the air loop gas stream through the NaOH in the bubbler tube. After a steady low value or zero carbon dioxide concentration was indicated on the recorder, the bubbler tube was valved out of the air loop, the air pump was shut off and the loop flushed with nitrogen gas to check the zero setting and to provide a zero gas in a desorption process. The NaOH in the bubbler tube was titrated with 0.1 N HCl to pH 7 using neutral red and a pH meter to check the end point. The bubbler tube was refilled with 10 ml of 0.2 N NaOH and flushed with nitrogen for 15 to 20 minutes. The air loop was then valved from the flushing gas and the air pump turned on. The carbon dioxide concentration in the air circulating gas stream was at zero on the IR carbon dioxide analyzer and the recorder. This zero gas air stream was then used to desorb the carbon dioxide from the sample solution and to trap desorbed carbon dioxide in the 0.2 N NaOH in the bubbler tube. This desorption process with the zero gas recirculating stream was performed with the cold finger condenser in the "H" cell which maintained the solution temperature at either 15° or 33°.

Initial runs with the bubbler tube containing 4.92% carbon dioxide in the air loop gas stream were used to obtain carbon dioxide concentration curves for an empty tube, for one with 25 ml of 0.1 N NaOH, and one with 25 ml of distilled water. These curves indicated the effectiveness of this technique for carbon dioxide trapping during the desorption process. Carbon dioxide trapping during a flow through nitrogen aeration of the absorber solution was tried initially but was found to be inadequate to measure desorbed carbon dioxide.

SECTION VI

RESULTS

1. CARBON DIOXIDE ABSORPTION STUDIES

The carbon dioxide absorption curves of the various solutions were derived from the actual curve sensed by the analyzers and recorded. These recorded curves were dampened waves with a start at the initial carbon dioxide content in the air loop and an ending which was smooth. Figure 3 illustrates such a dampened wave. The carbon dioxide absorption curves were drawn from these waves by connecting the maxima of the peaks as indicated in the figure. Since a constant carbon dioxide content was initially present and a constant carbon dioxide content was indicated after a 10- to 15-minute period, these drawn carbon dioxide absorption curves were an adequate presentation of the change of carbon dioxide content in the air loop with time. This method was used for the carbon dioxide absorption curves for 270 ppm carbon dioxide in nitrogen, for 0.4% carbon dioxide in air, the 5.0% carbon dioxide in nitrogen, and 4.92% carbon dioxide in air.

The three absorption cells, the "H" cell, the midvale bulbs and the bubbler tube (sketched in Figure 1) were run empty, with distilled water, and with the various absorbers, providing comparative curves. Figure 4 shows the "H" cell curves for an empty cell, for distilled water, and for 0.004 N NaOH. These are typical curves indicating fairly stable carbon dioxide values after 12 minutes. Arbitrarily, the carbon dioxide values at 20 minutes were compared for capacities and absorber effectiveness. The time intervals to attain a stable value not changing more than 2 mm/3 min time interval was considered the basis for comparing the efficiencies as to carbon dioxide absorption. The curves for the evaluation of the midvale bulbs as an absorption train in Figure 5 were consistent with those obtained with the "H" cell but were not as effective, comparing specifically the NaOH at 0.1 N curve 2 in the midvale bulb with the NaOH at 0.0004 N in the "H" cell curve 3 (Figure 4). On this basis, the midvale bulbs were replaced with the bubbler tube (Figure 2) that had an extra coarse glass plug gas diffuser. Curve 4 in Figure 5 shows continuous absorption of the residual CO_2 of curve 3 in another 25 ml aliquot of NaOH.

The carbon dioxide absorption curves for the gas bubbler tube in Figure 6 show the curves for NaOH, $\text{Ba}(\text{OH})_2$, and monoethanolamine (MEA). The $\text{Ba}(\text{OH})_2$ solution was discontinued as a comparative absorber because the carbonate formed gradually plugged the ground glass gas diffuser and resulted in an increase in the pressure drop across the absorption cell. Glass beads in the bubbler tube did not effectively increase the carbon dioxide absorption, comparing curves 2 and 3 in Figure 6. The MEA absorption curve verified previous work on the effectiveness of MEA for carbon dioxide absorption, but was not considered applicable for CO_2 trapping.

A comparison of tris solution and sodium carbonate as to carbon dioxide absorption from 0.4% carbon dioxide in air in the "H" cell is presented in Figure 7. Curve 1 for tris at 0.02 M was similar to the curve obtained for sodium carbonate. The addition of the enzyme to tris and to sodium carbonate revealed a catalysis of carbon dioxide absorption as shown by curves 3 of Figures 5 and 7.

The effectiveness of tris for carbon dioxide absorption was further compared under the various test conditions in Figure 8. Tris at 0.1 M with and without CA and at 14° and 25°, and at 0.05 M at 25° and 33° produced carbon dioxide absorption curves which showed that at the lower temperature, tris plus CA had a greater capacity for carbon dioxide. This was evident when comparing curves 3, 4 and 5 in Figure 8. The effect of tris concentration on carbon

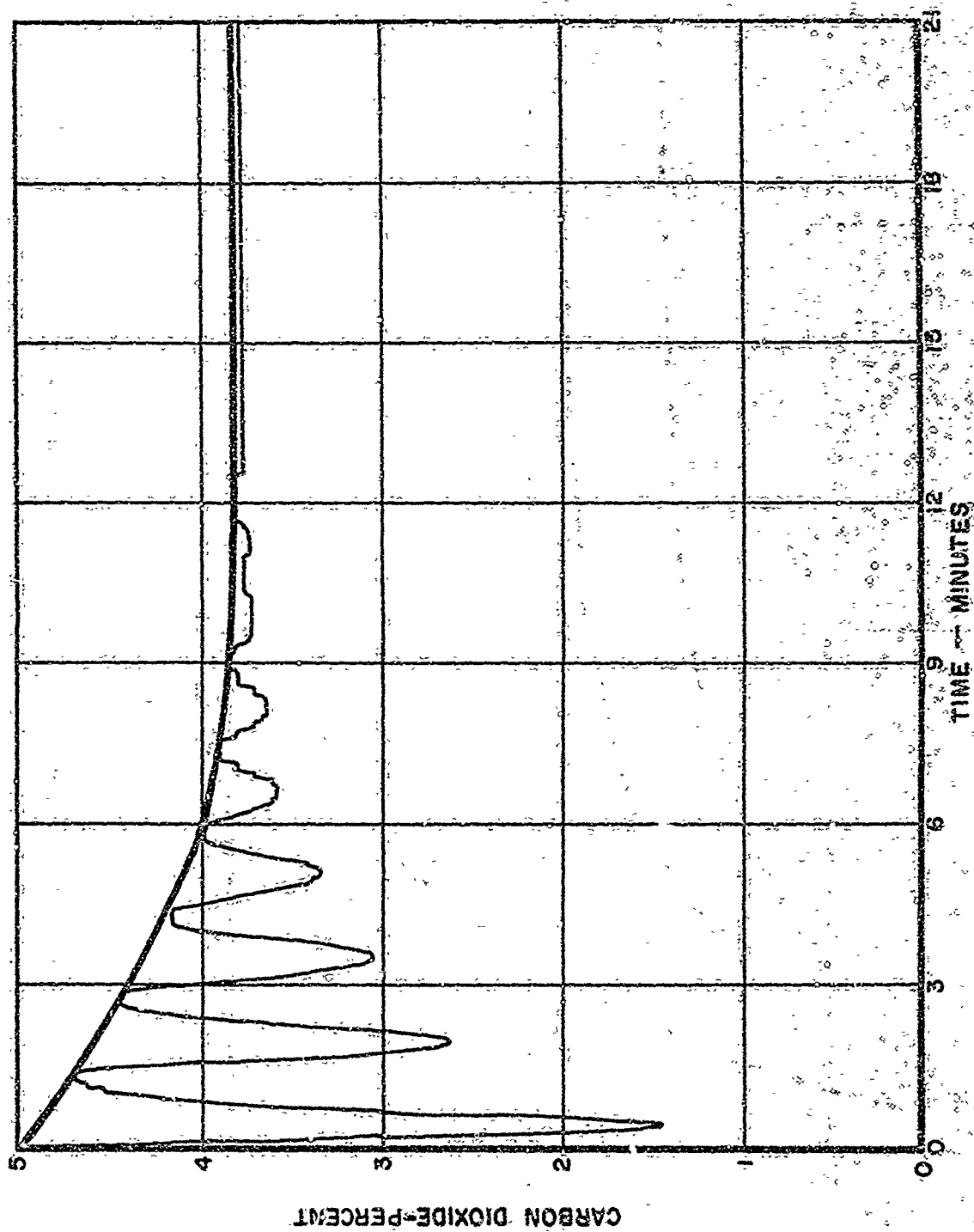


Figure 3. Method of Obtaining the CO_2 Percent Versus Time Curve With the Empty Bubbler Tube

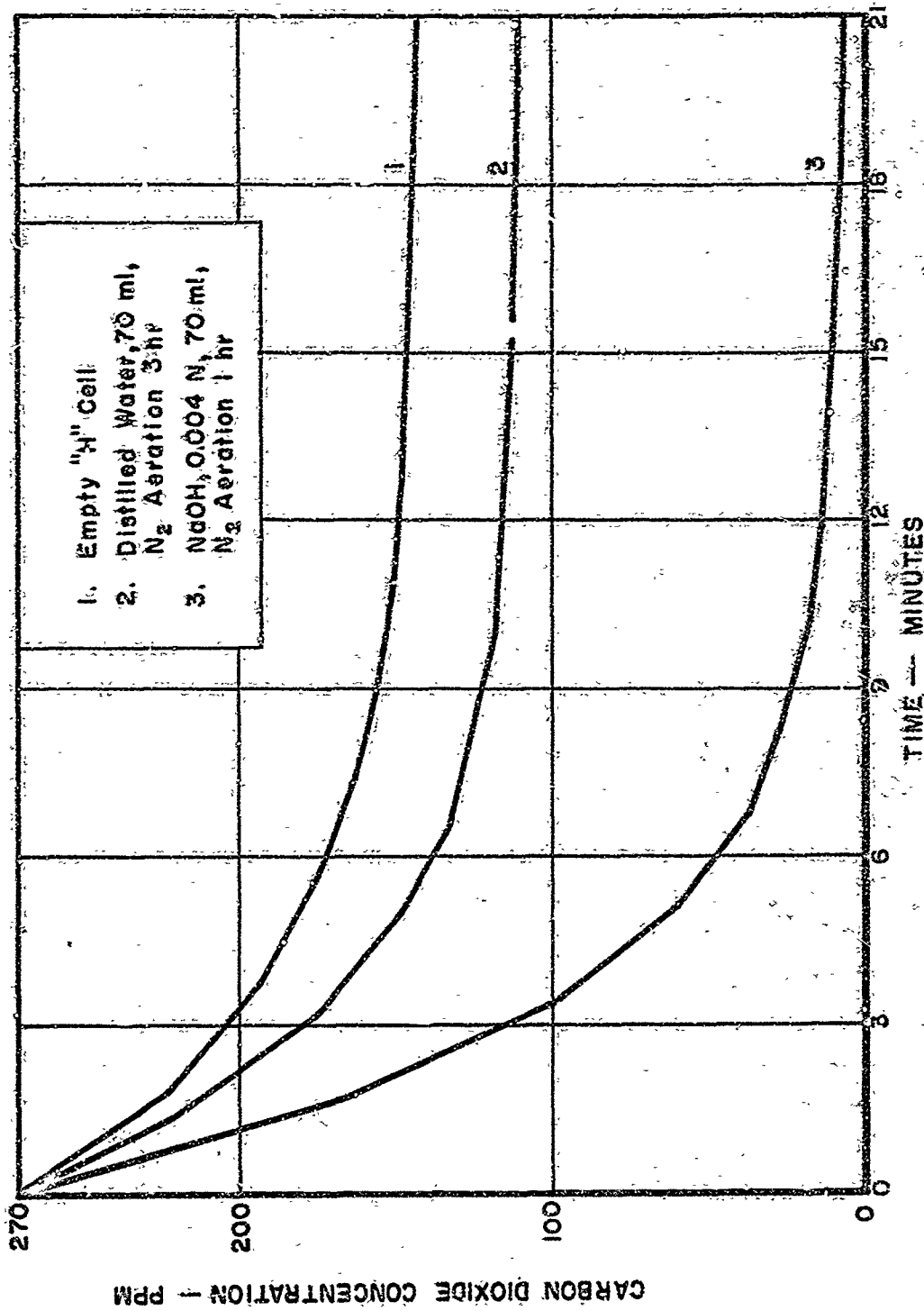


Figure 4. Comparative CO₂ Change Curves Using the "H" Cell

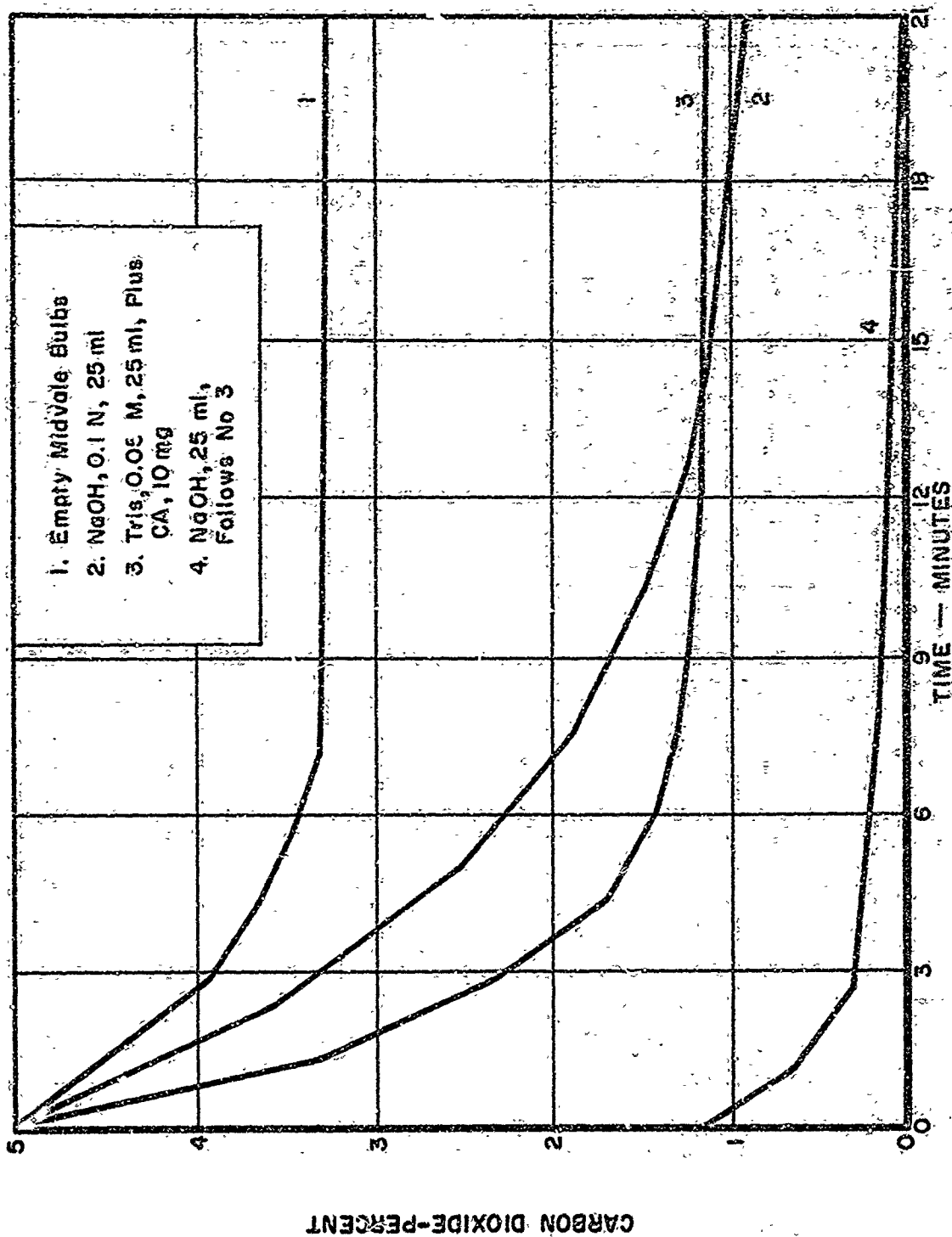


Figure 5. CO₂ Absorption Curves Using Midvale Bulbs

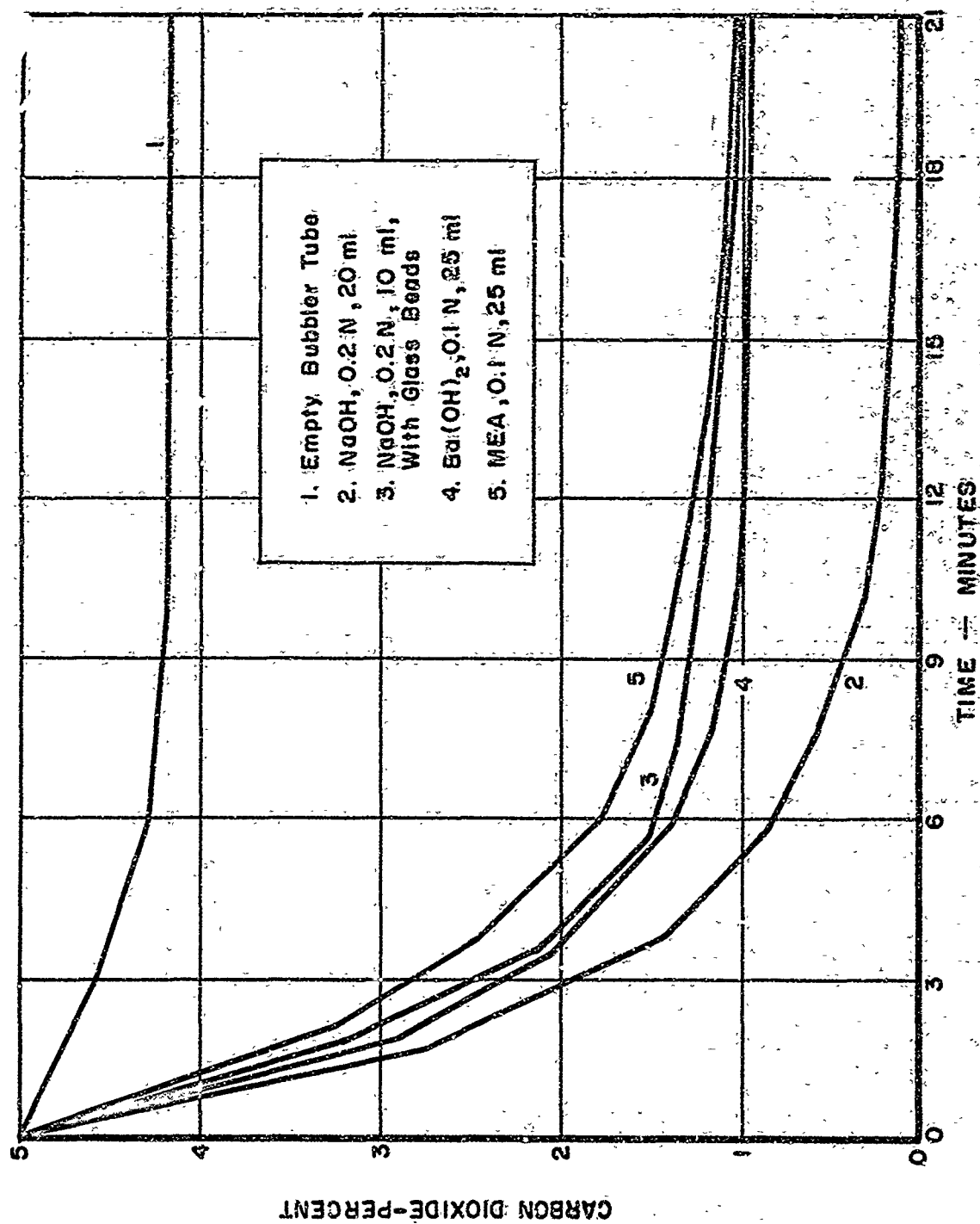


Figure 6. Comparison of CO₂ Change Curves for Standard Absorbers, Using the Bubbler Tube

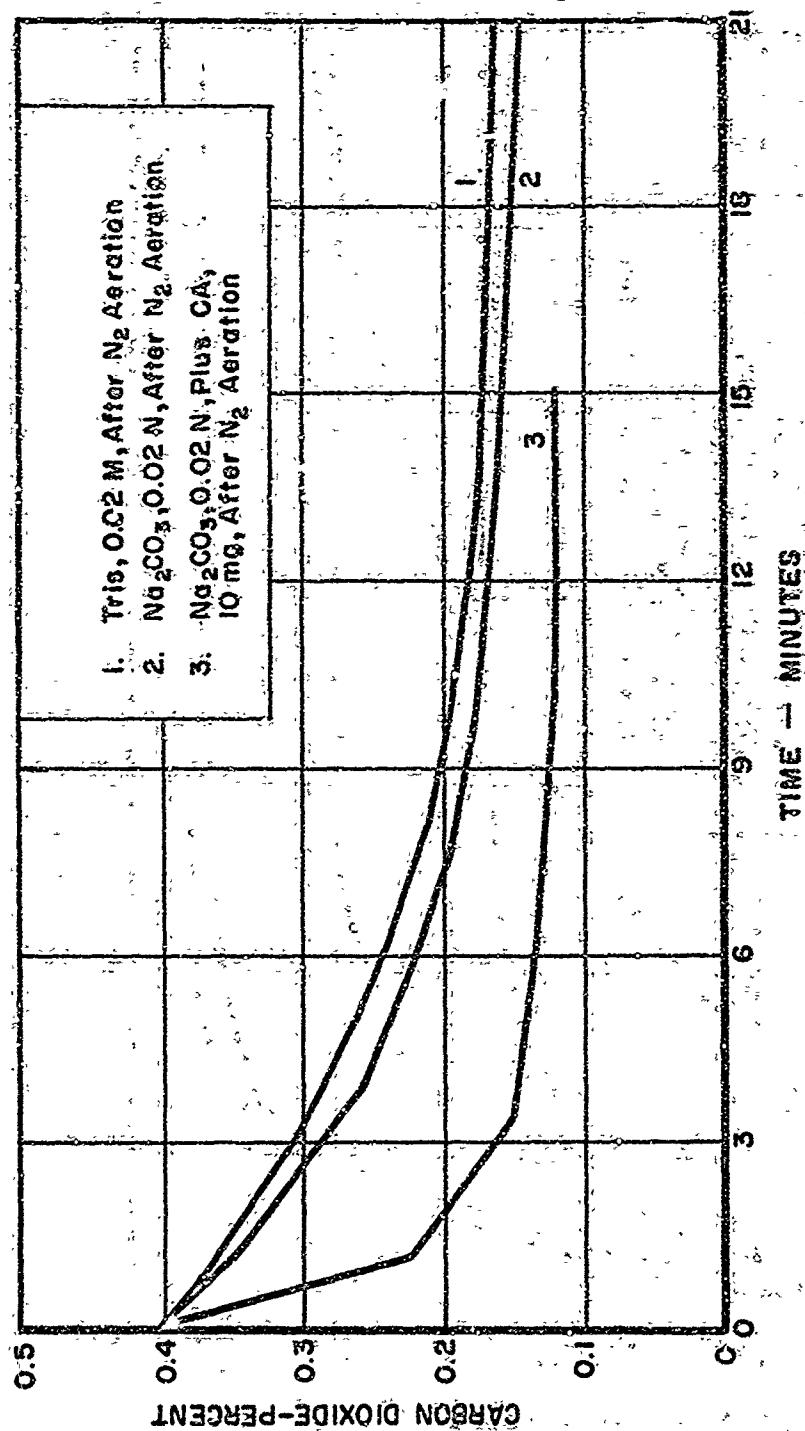


Figure 7. Comparison of Tris and Na_2CO_3 CO_2 Absorption Curves in H_2O Cell

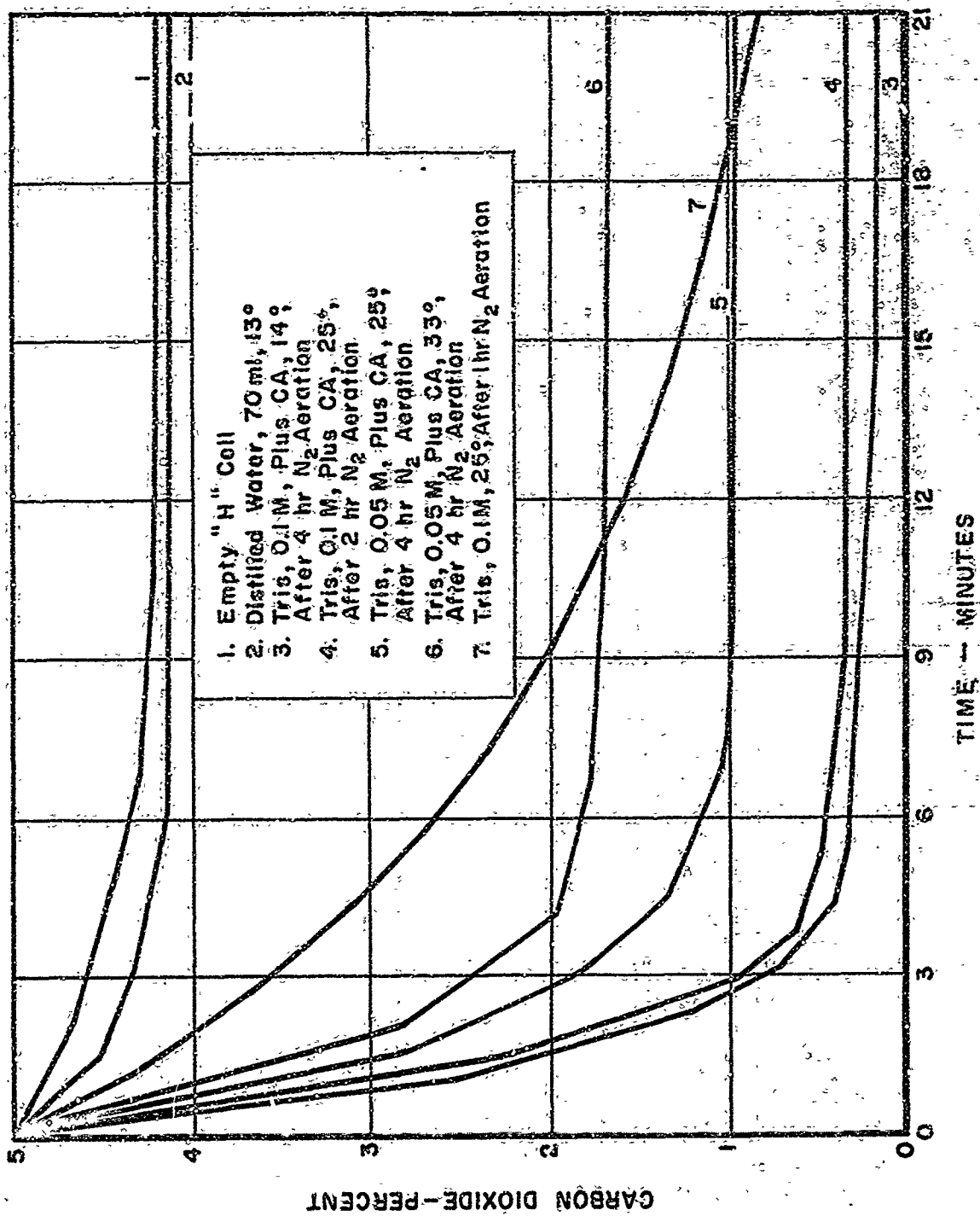


Figure 8. CO₂ Absorption Curves for Tris Solutions, 0.05 and 0.1 M. With CA at 13°, 25°, and 33°, 70 ml Solution in "H" Cell

dioxide absorption may also be compared in curves 4 and 5. Tris at 0.1 M plus CA was effective in carbon dioxide removal up to 97% in a 15-minute recycle time. This carbon dioxide was releasable from the tris solution by merely changing the temperature of the solution as shown in Figure 9. The tris plus CA at 13° was used in an absorption run and indicated 84% carbon dioxide removal compared with 58% carbon dioxide removal for tris at 34°. By a change in temperature of the tris solution, its capacity was increased or decreased, the carbon dioxide change indicated in curves 1 and 2 of Figure 9, beginning at either 13° or 34°. This temperature cycling was effective and consistent, as evidenced by the identical carbon dioxide content attained upon the same temperatures of the solution. From curve 1 a change of 19° corresponded to a change from 1.66% carbon dioxide to 0.93% carbon dioxide in the circulating air or 0.73% of the carbon dioxide removed. This same amount of change, 0.73% carbon dioxide, was also obtained from curve 2 whether on the heating or cooling portion of the individual curves. It was significant here that the same solution was used for both curves, curve 2 being obtained after a 16-hour resting period followed by 4 hours of nitrogen aeration at 34°. The problems met here concerned the heating of the enzyme solution. The heater surface temperature must not exceed the temperature of enzyme inactivation which was quite low. In this work, the temperature of the recirculating hot water was 45° for attaining 34° and 32.5° temperatures in the enzyme-tris solution. Recirculating water at 55° was needed to attain a 40° temperature in the tris solution. However, the carbon dioxide absorption curves obtained for the tris plus enzyme solution showed typically a tris absorption curve after this temperature was attained in the enzyme-tris solution.

Tris-maleate (TM) buffer was evaluated as a carbon dioxide absorber from the curves in Figure 10 and 11 with 0.4% CO₂ in air and 5.6% CO₂ in nitrogen.

TM plus CA solution, however, foamed excessively so that reduced nitrogen aeration rates of 250 cc/min were used for regeneration and 0.6 cfm (285 cc/min) in the air loop. The effect of an applied DC potential on the "H" cell during an air loop run revealed an accelerating effect with 10 v DC applied with a negative potential at the bubbler tube. In comparing curves 4 and 5 with 3, in Figure 10, a definite change may be seen indicating that an applied potential enhanced carbon dioxide absorption and desorption. At the 15-minute time interval in Figure 10 where curve 1 of TM crosses curve 3 of TM plus CA, the carbon dioxide in the air loop amounted to 1.59% with 61% of the carbon dioxide removed. The TM plus CA with a 10 v DC potential negative at the bubbler tube indicated an increase in carbon dioxide absorption capacity. Curve 5 of Figure 10 showed 63% of the carbon dioxide in the air loop removed.

2. CARBON DIOXIDE DESORPTION STUDIES

Regeneration of carbon dioxide absorption capacity of tris plus CA was accomplished by long periods of nitrogen aeration at room ambient conditions. The curves in Figures 12 and 13 show the effectiveness of this method. The use of a vacuum of 28 in. of Hg for 5-minute periods did not increase the capacity but did indicate possibly an increased rate as evidenced by curve 3 in Figure 13. The pH of the tris plus enzyme solution in Figure 14 indicates an initial lag in the recovery to its original pH but then indicates a regenerated solution as to pH.

The effect of the application of an electrical potential to the tris solution plus CA in the "H" cell during nitrogen aeration revealed an enhanced pH regeneration as in curve 2 in Figure 15 but the subsequent carbon dioxide absorption curves, 2 and 3 in Figure 12 did not reveal this positive effect as to capacity regeneration. The time of nitrogen aeration between carbon dioxide absorption runs was significant. There was an apparent crossing over of the carbon dioxide absorption curves in the initial five minutes in Figure 12. This was significant since this indicated an accelerated rate for those curves in which an applied potential was used. The time of nitrogen aeration between curves 2 and 3 was only 20 minutes compared with the 60 minutes between curves 1 and 2. Curve 4 was obtained after the regeneration runs with applied voltage periods and a total nitrogen aeration time of five hours. The application of a DC potential had a positive effect on this regeneration process.

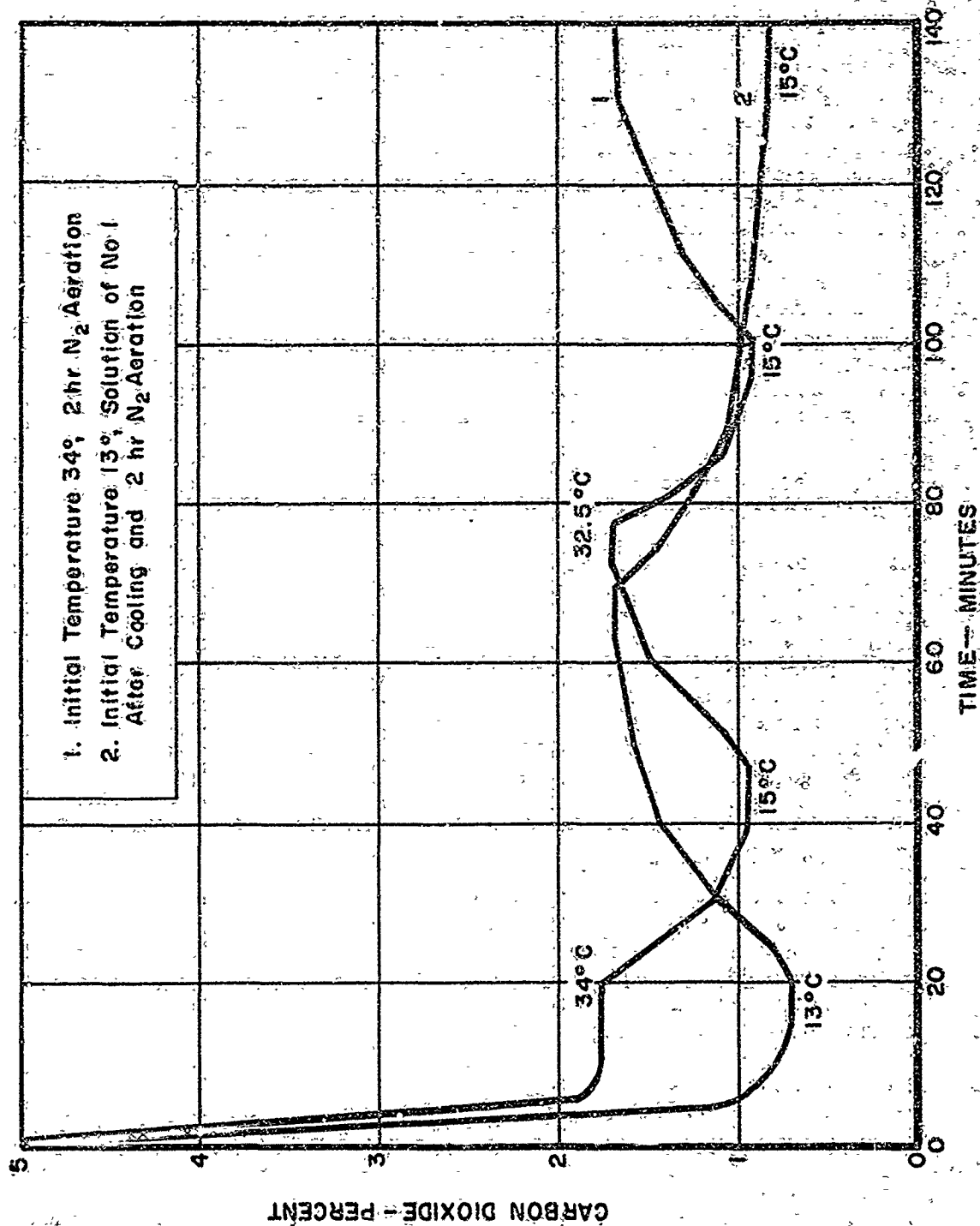
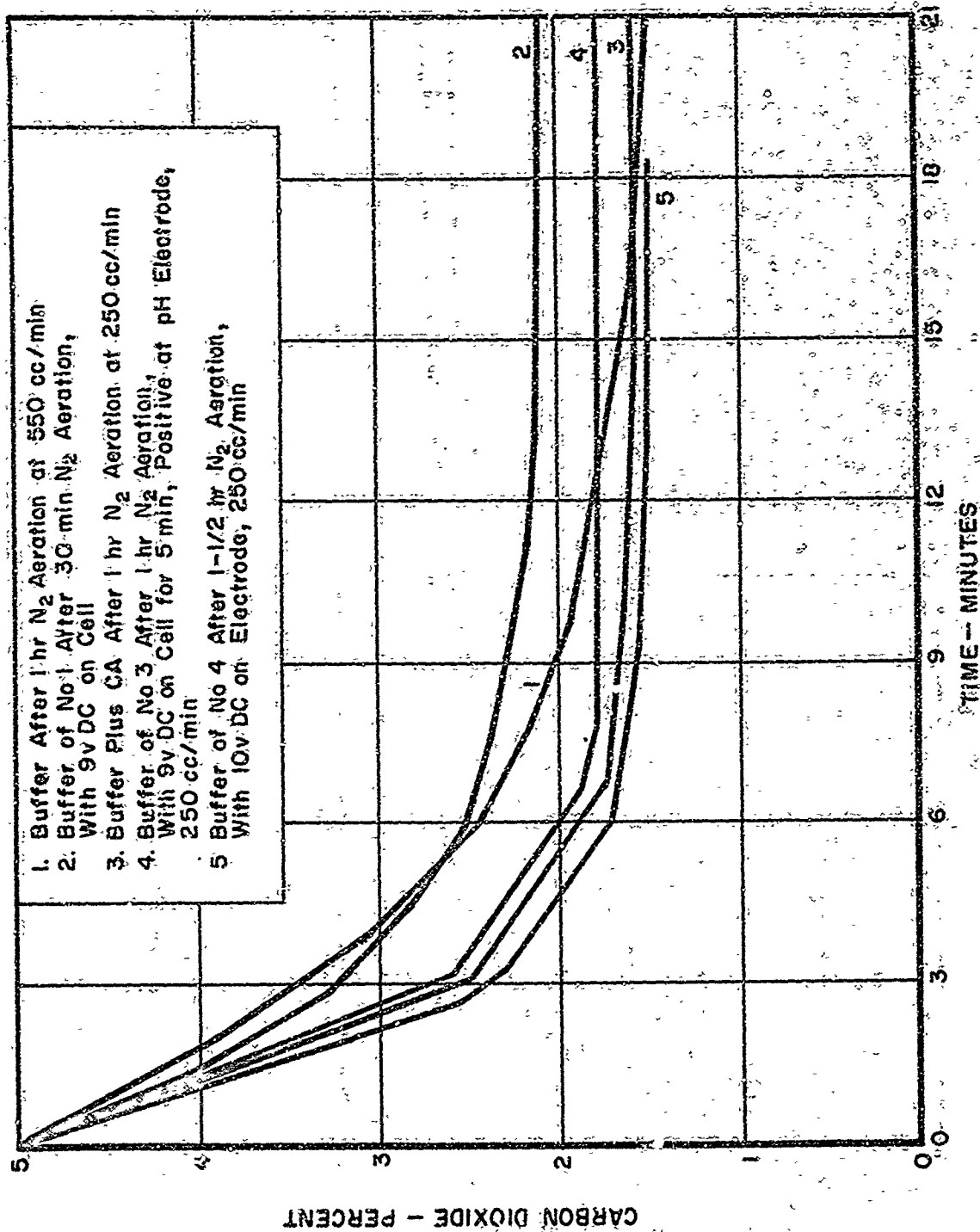


Figure 9. Temperature Cycling Effect on CO₂ Retention in Tris Solution, 0.05 M, Plus CA

Figure 10. TM Buffer, 0.02 M, CO₂ Absorption Curves, 70 ml in "H" Cell.

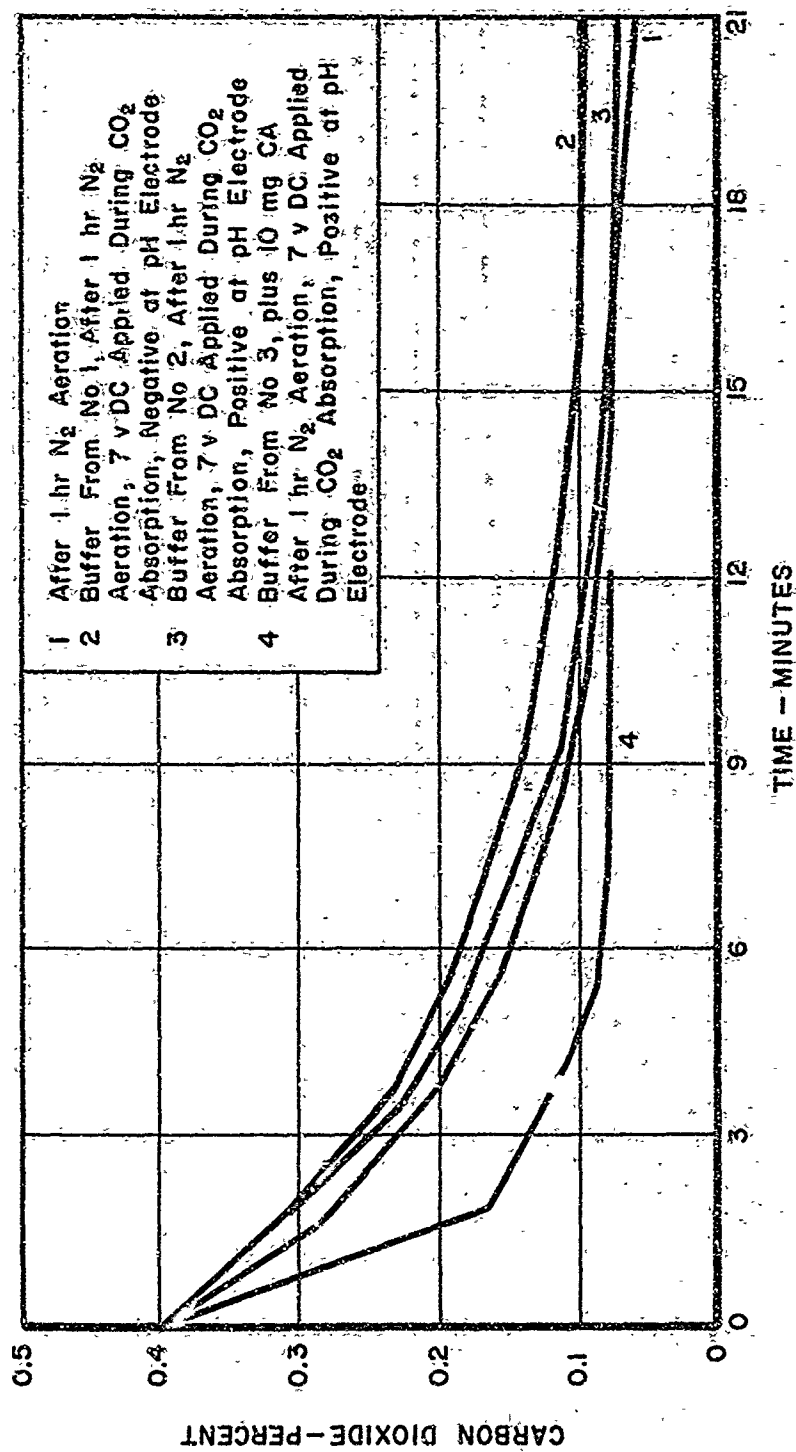


Figure 11. CO₂ Absorption Curves for TM, 0.02 M, 70 ml in 'H' Cell With 7 v DC Applied

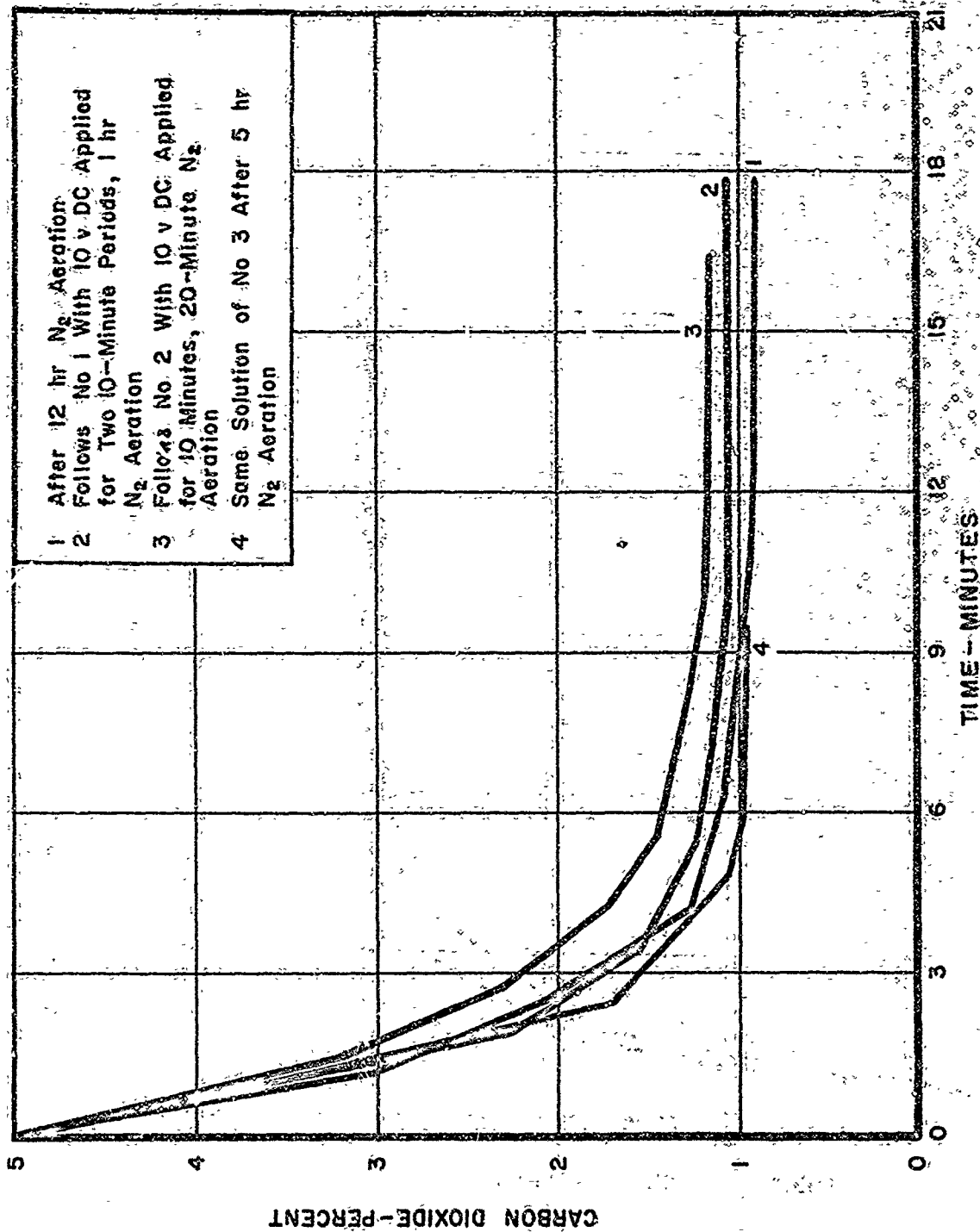


Figure 12. Regeneration of CO_2 Absorption Capacity of Tris Solution, 0.05 M, Plus CA by N_2 Aeration and Applied DC Potential

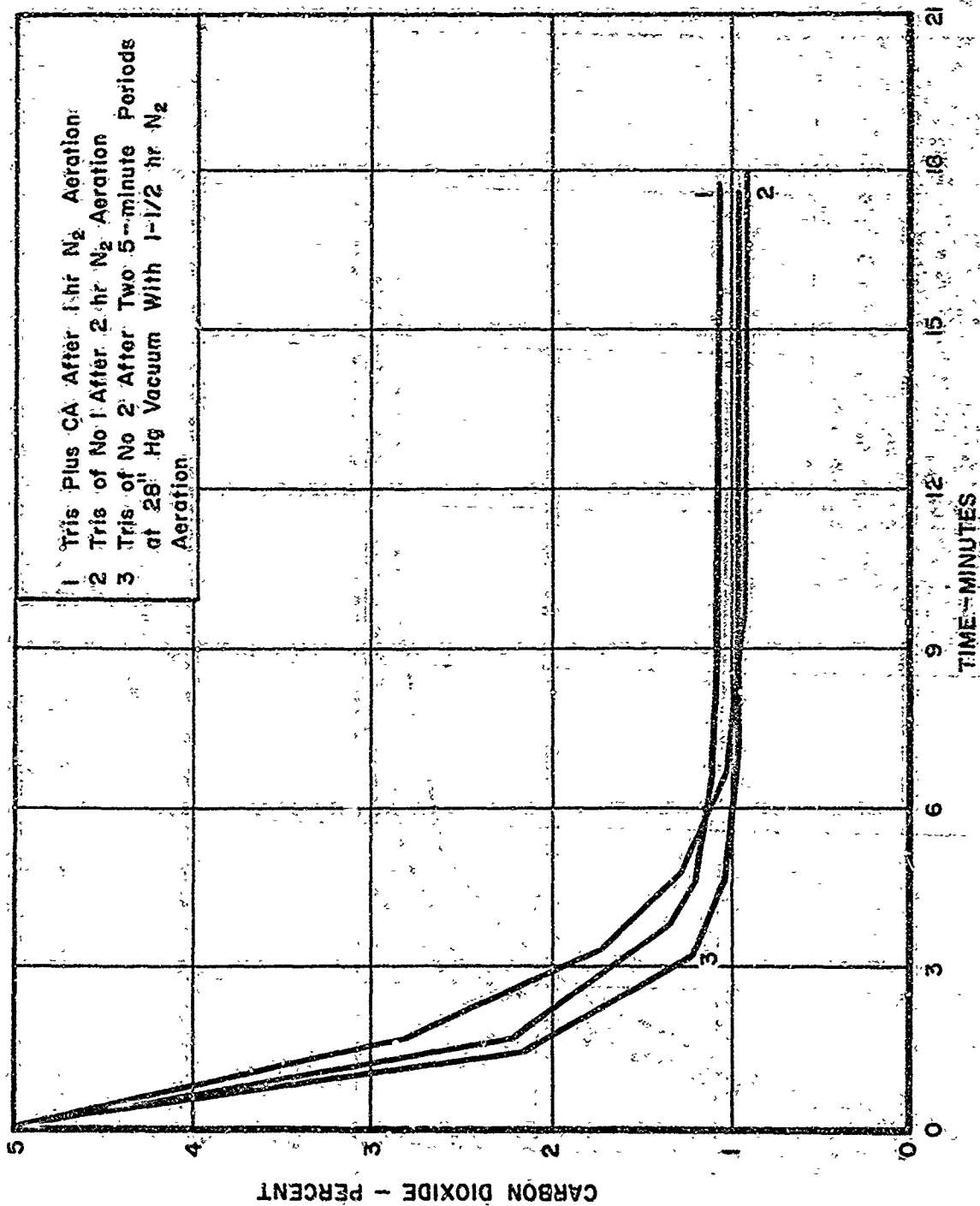


Figure 13. Tris Solution, 0.05-M, With CA CO₂ Absorption Following N₂ Aeration and With Vacuum.

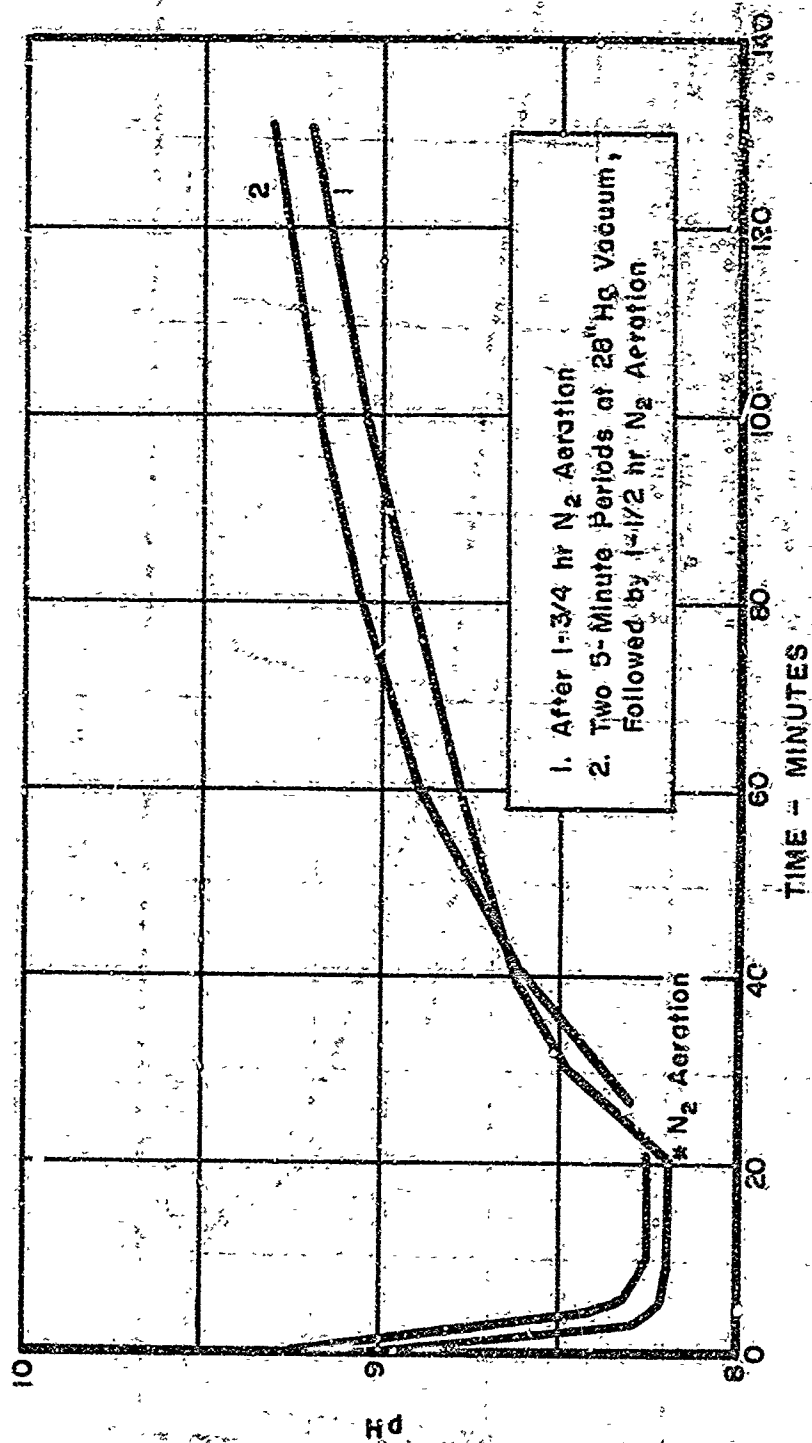


Figure 14. pH Change of Tris Solution, 0.05 M, With GA During N₂ Aeration

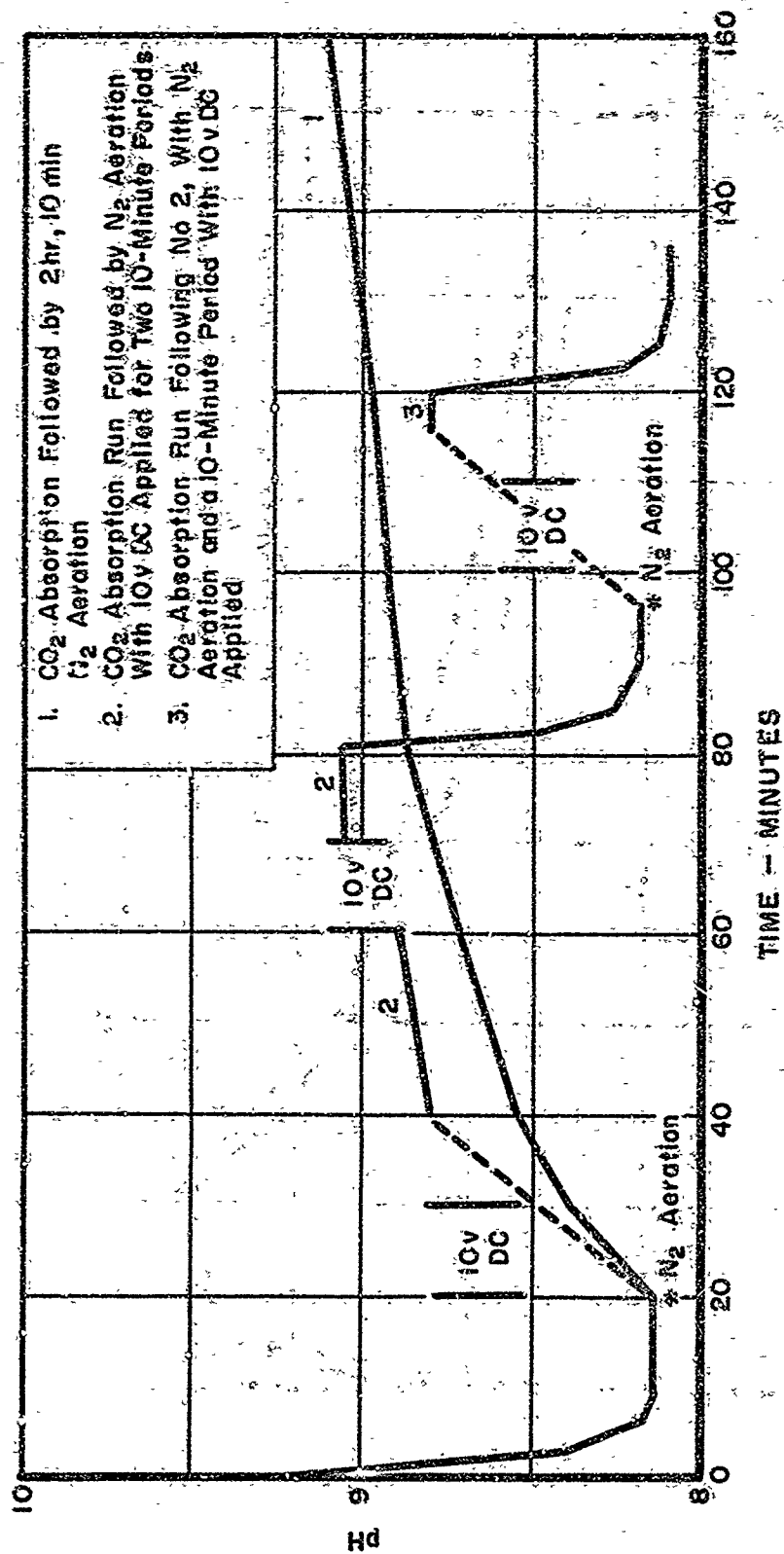


Figure 15. Comparison of pH Changes in Tris Solution, 0.05 M, Plus CA During a CO₂ Absorption Run Followed by N₂ Aeration With a DC Potential Applied to the Cell

3. pH CHANGES

The pH changes in the tris solutions during carbon dioxide aeration were not significant when the carbon dioxide at 270 ppm in nitrogen was used as the recirculating gas in the air loop. A change of from 9.40 to 9.35 pH and from 9.45 to 9.40 pH was measured in runs with tris at 0.05 M and tris 0.05 plus CA even though the carbon dioxide reduction was significant in the carbon dioxide absorption curves 3 and 4 in Figure 16. This reduction in carbon dioxide content was at 20 minutes based on the empty cell curve down to 40 ppm from an initial 226 ppm CO_2 content when tris plus CA was used as indicated by curve 4.

This was an 83% reduction in the carbon dioxide content with only a 0.05 change in the pH. However, when 5.0% or 0.4% carbon dioxide was used in the flow-through method of aeration, the pH changes were greater as shown in Figure 17. These pH changes ranged from 0.9 to 1.4 units and depended upon the initial pH and the absorber concentration. The pH changes of tris at 0.1 M during air loop runs are indicated in Figure 18, curve 1 for three consecutive air loop runs using 5.0% carbon dioxide in nitrogen in the air loop. These air loop runs, shown in Figure 19, reveal a saturation effect on the absorber and, concurrently, a smaller change of pH during the absorption process. Other curves showing pH change in tris with and without the enzyme are presented in Figures 20, 21, and 22.

The pH changes in MEA during carbon dioxide aeration are indicated in Figure 23. These pH changes were all steep and were stabilized at a low value when CA was present.

Regeneration of the carbon dioxide absorption capacity of the tris absorber with and without the enzyme was accomplished with long nitrogen aeration as indicated in curve 1 of Figure 14 and 20 in which the initial pH was attained in the solution. The subsequent carbon dioxide absorption run in the air loop of tris in another comparable series of carbon dioxide absorption runs with no nitrogen aeration between runs are indicated in Figure 24, curves 2, 3, 4, and 5. Curve 6 in Figure 24 provided a comparison as to the specific effects of enzyme catalysis of carbon dioxide absorption by tris after temperature inactivation of the enzyme.

Regeneration of the pH by nitrogen aeration was not enhanced by the addition of selenite, an ion reported as having an accelerating effect on hydration of carbon dioxide activity. Nitrogen aeration revealed no significant increase in the pH change over that using only tris and the enzyme as in Figure 25. The tris plus enzyme solution showed a greater rate of pH change than was evident when only tris was aerated with nitrogen.

Regeneration of pH and the CO_2 absorption capacity with the application of a vacuum of 28 in. of Hg for the two 5-minute periods and using nitrogen as a bubbling gas indicated (Figure 14) a somewhat delayed effect for pH change. This delay was for 30 minutes or so, but after the initial delay, the pH in the solution exposed to vacuum recovered to a value above that initially used. This effect was not unexpected since the tris solution was one reused. This effect was compared to that in Figure 22 indicating pH recovery with a used solution in curve 1. Curve 2 showed pH changes for a freshly prepared solution which was not as great as with nitrogen aeration. This effect on freshly prepared solution was rationalized as a "needed seasoning" process also observed by Graf's work (Reference 3).

With MEA, pH recovery by nitrogen aeration (Figure 23) showed the catalytic effect for carbon dioxide absorption and desorption, but because of excessive foaming aeration rates were not comparable. Both curves initially had pH's of 11.25.

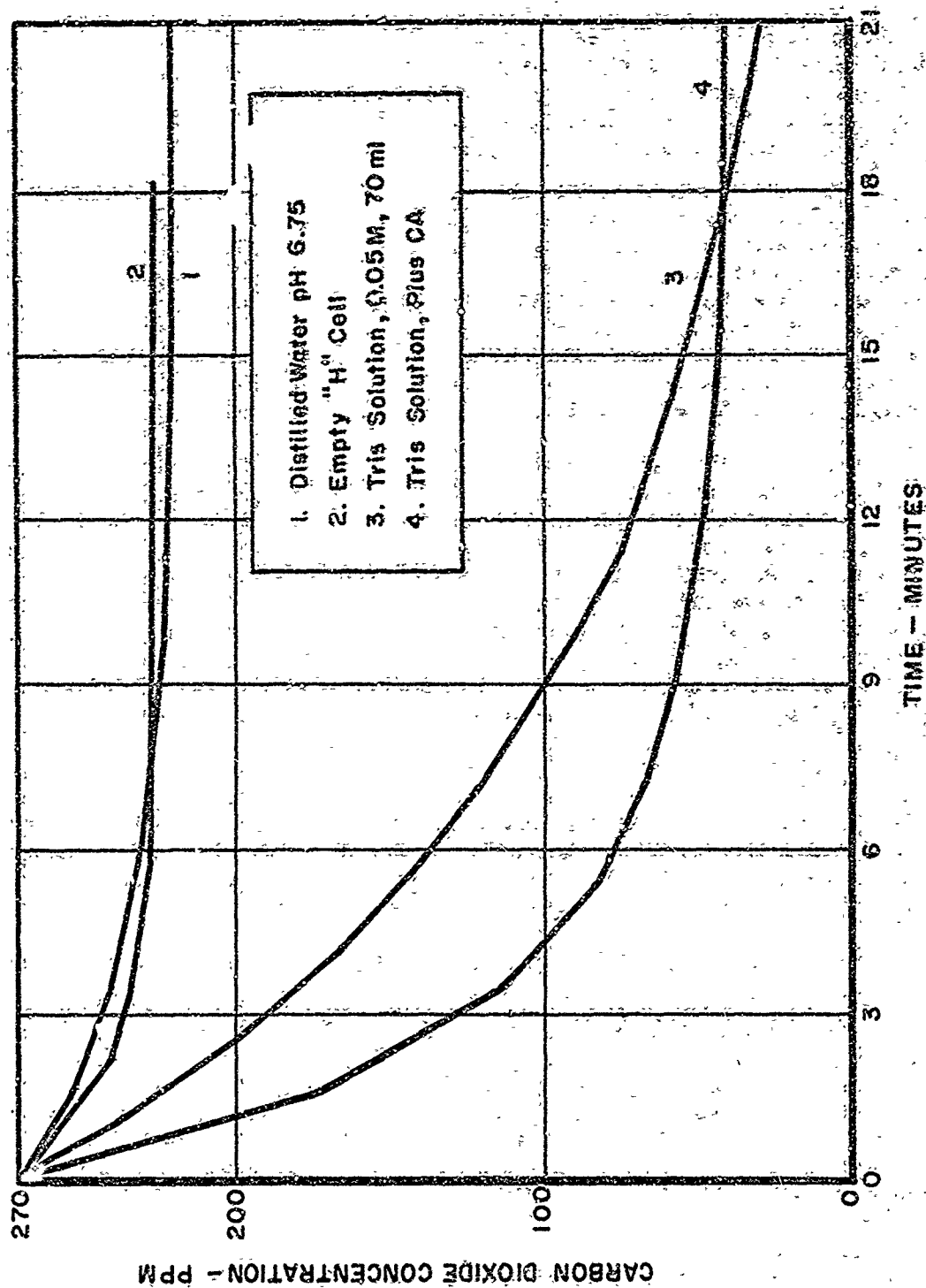


Figure 16. CO₂ Absorption Curves of Tris Solution, 0.05 M, Using Low Concentrations of CO₂

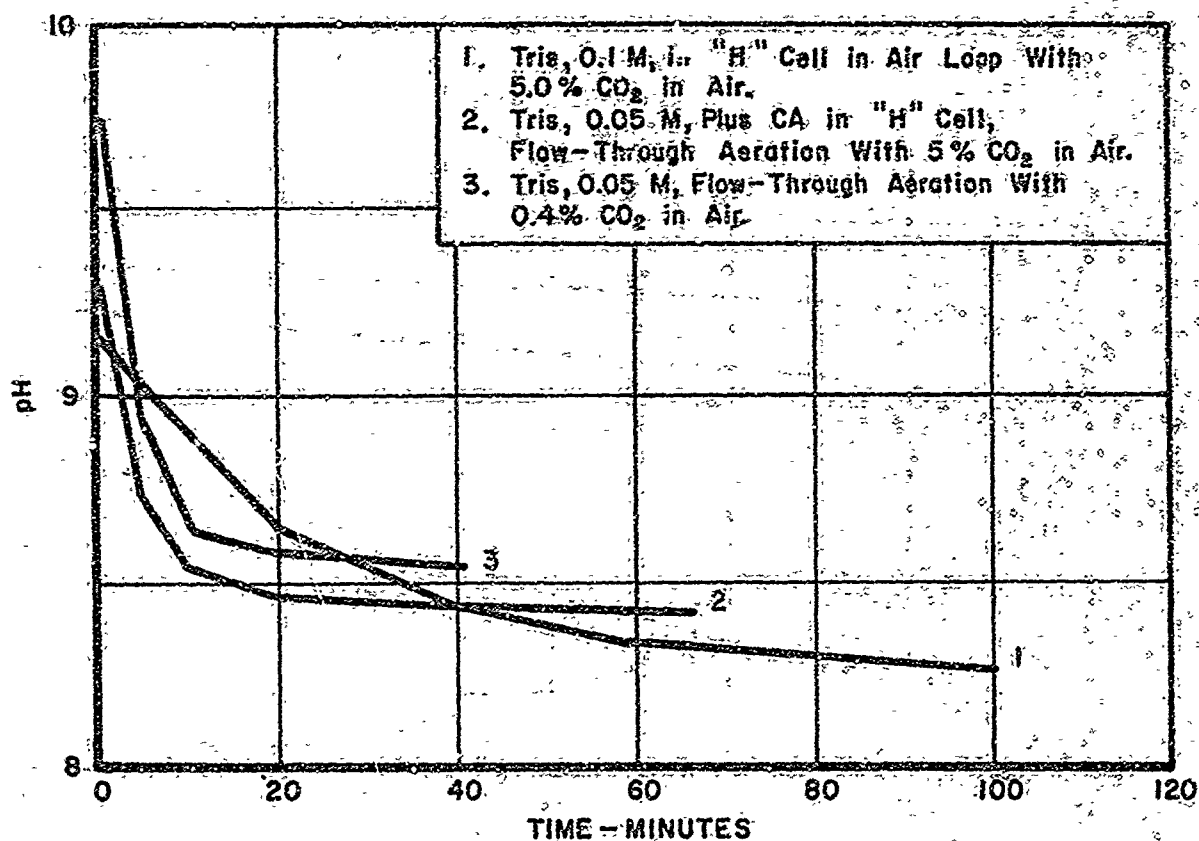


Figure 17. Change of pH of Tris Solution When Aerated With Different CO₂ Percentages

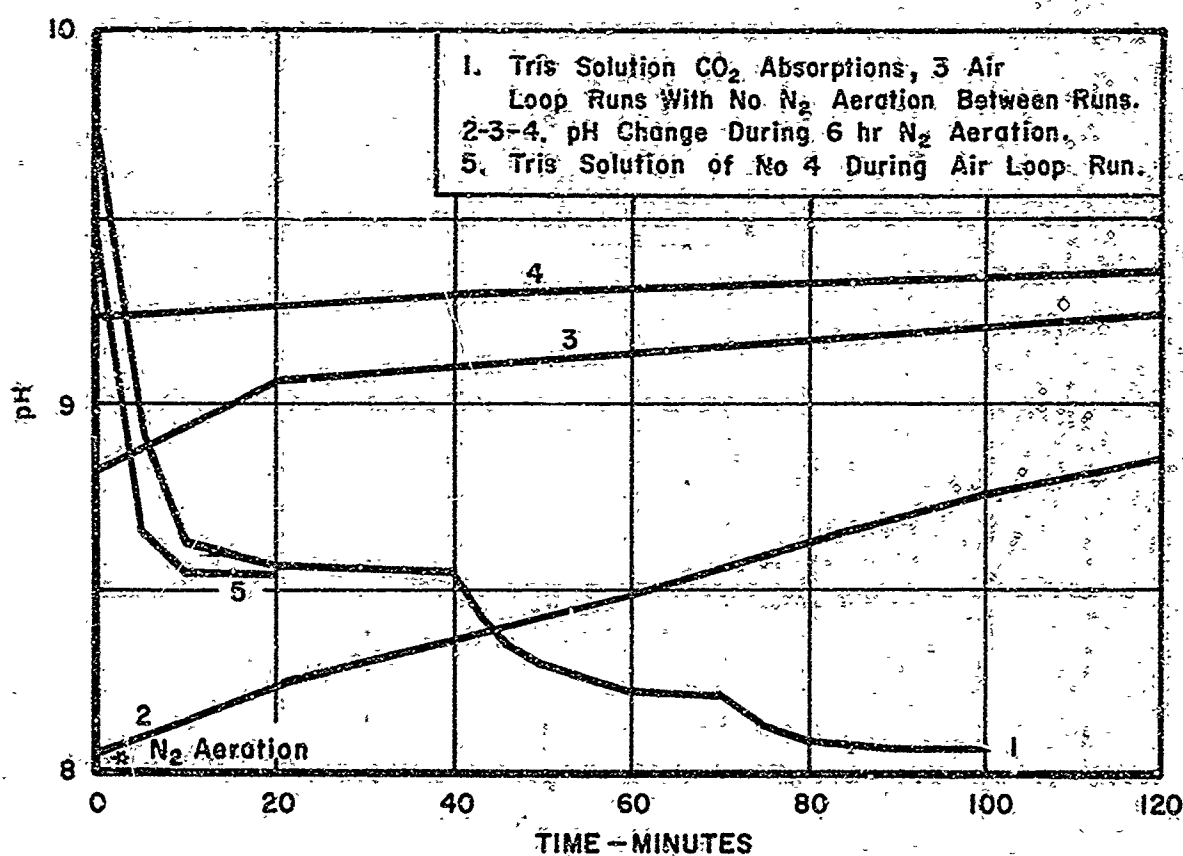


Figure 18. Change of pH of Tris Solution, 0.1 M, During CO_2 Absorption Runs in Air Loop and Subsequent N_2 Aeration

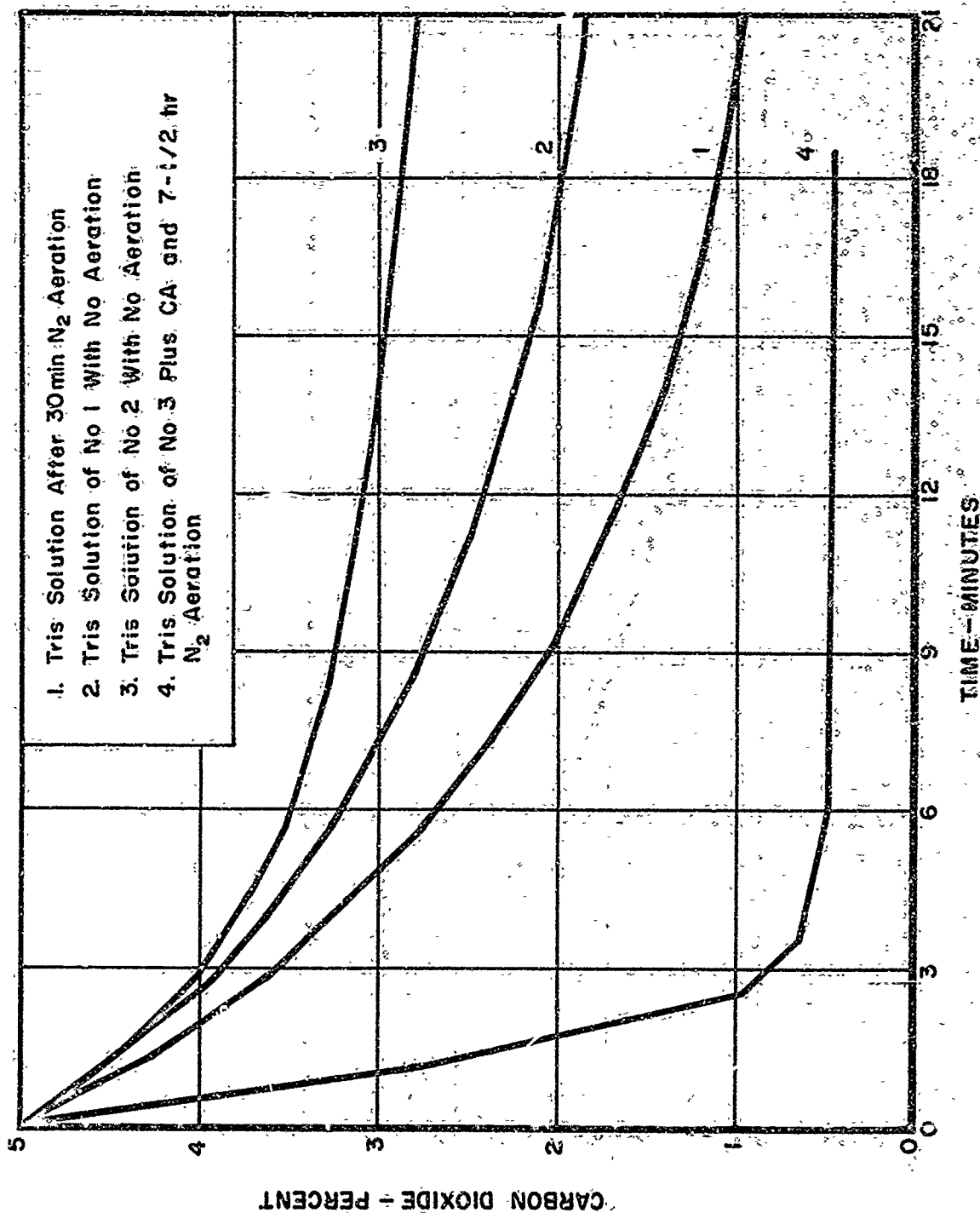


Figure 19. CO₂ Absorption Runs With 70 ml Tris, 0.1 M, in 7H⁺ Cell Showing Effect of N₂ Aeration Between Runs

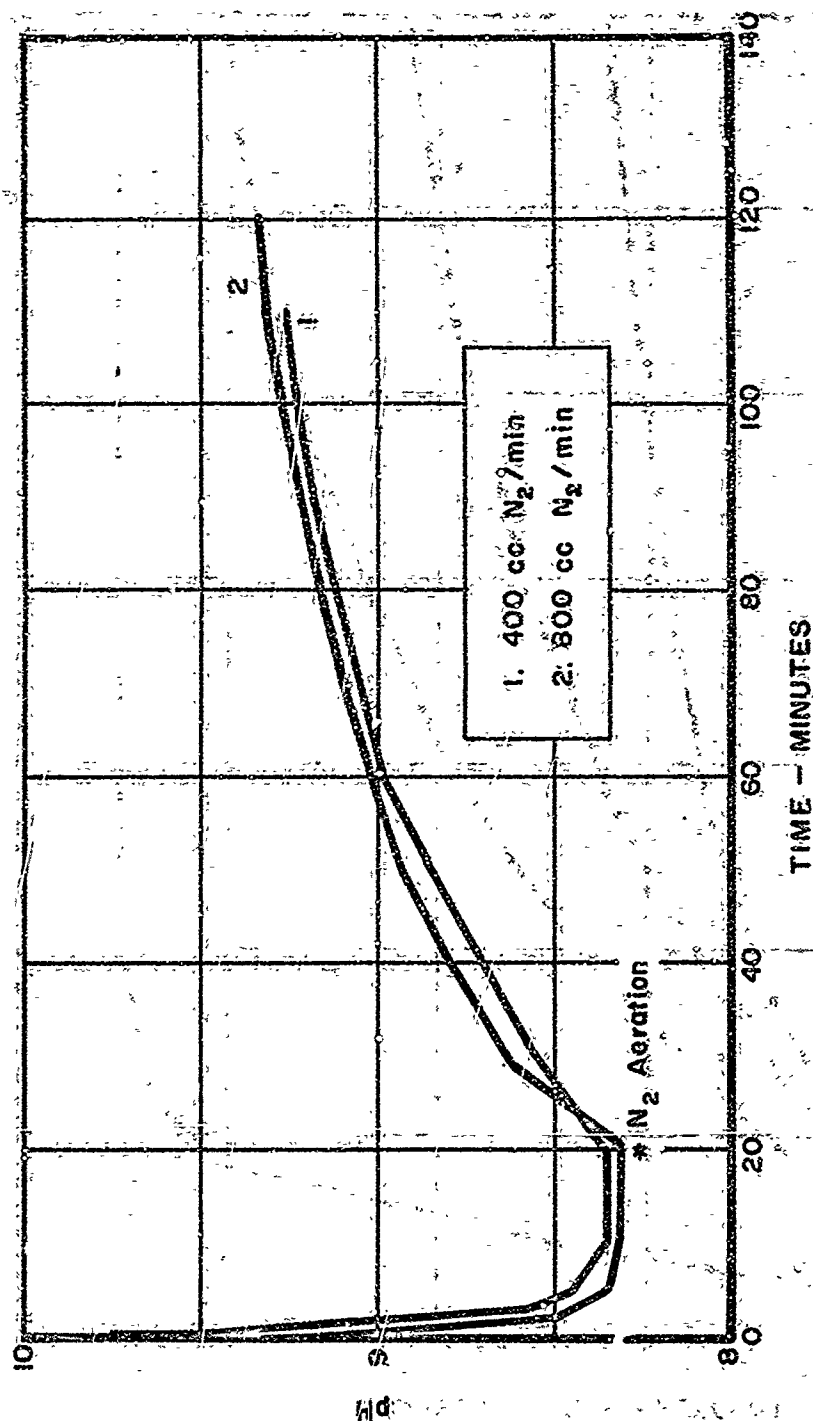


Figure 20. Effect of N₂ Flow Rate on pH Change in Tris Solution, 0.05 M, Plus OA

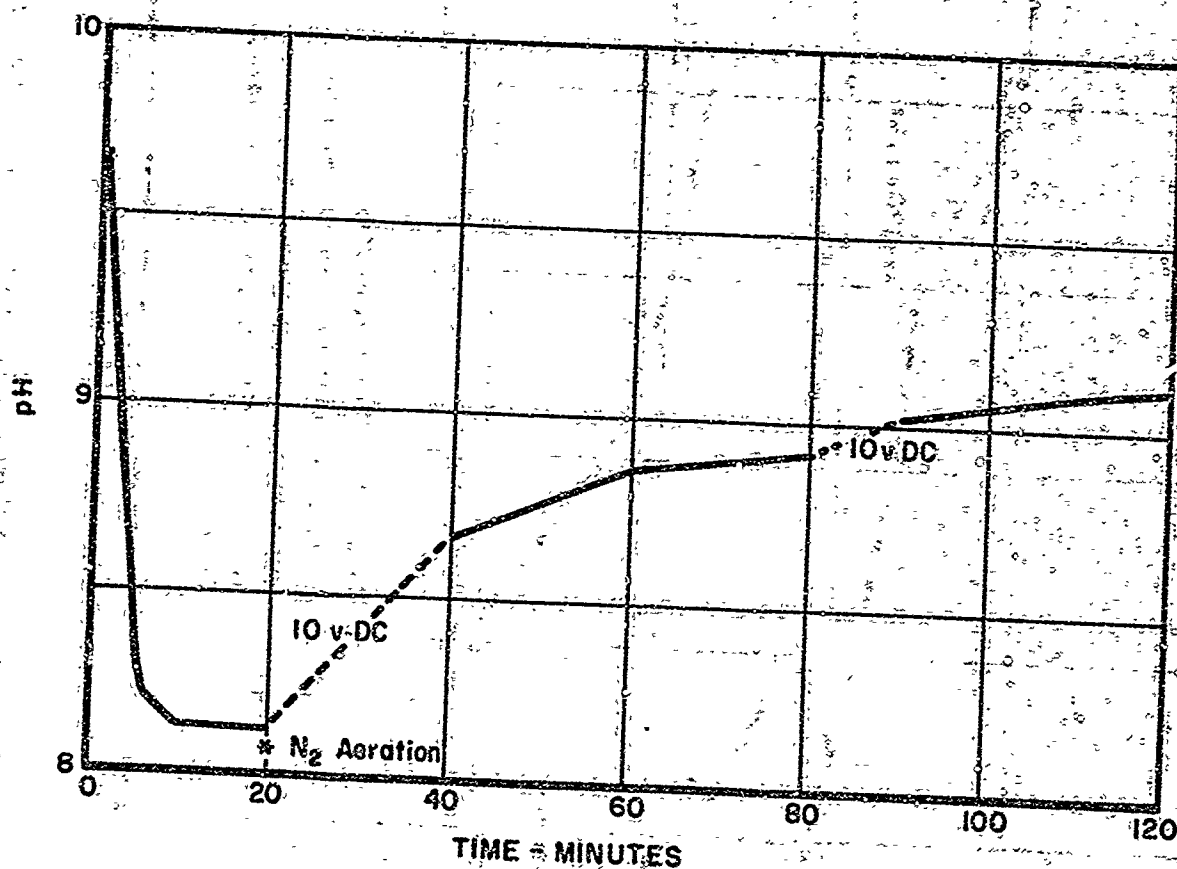


Figure 21. Change of pH of Tris Solution, 0.05 M, Plus CA During CO₂ Absorption Run Followed by Two 10-Minute Periods of 10v DC During N₂ 1 Hour, 40 Minutes N₂ Aeration

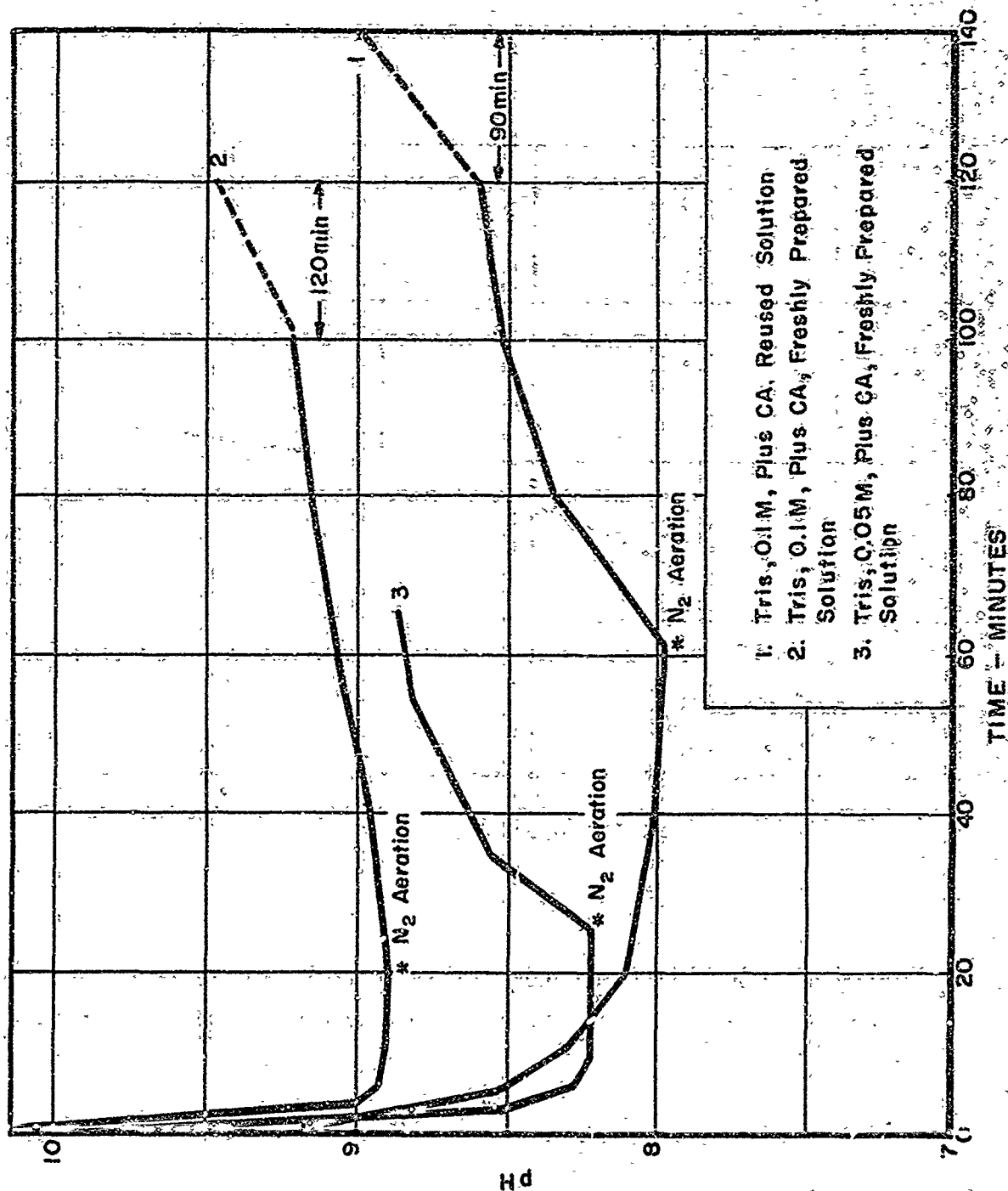


Figure 22. pH Change of Tris Solution Plus CA During CO₂ Absorption in Air Loop Run, and Subsequent N₂ Aeration

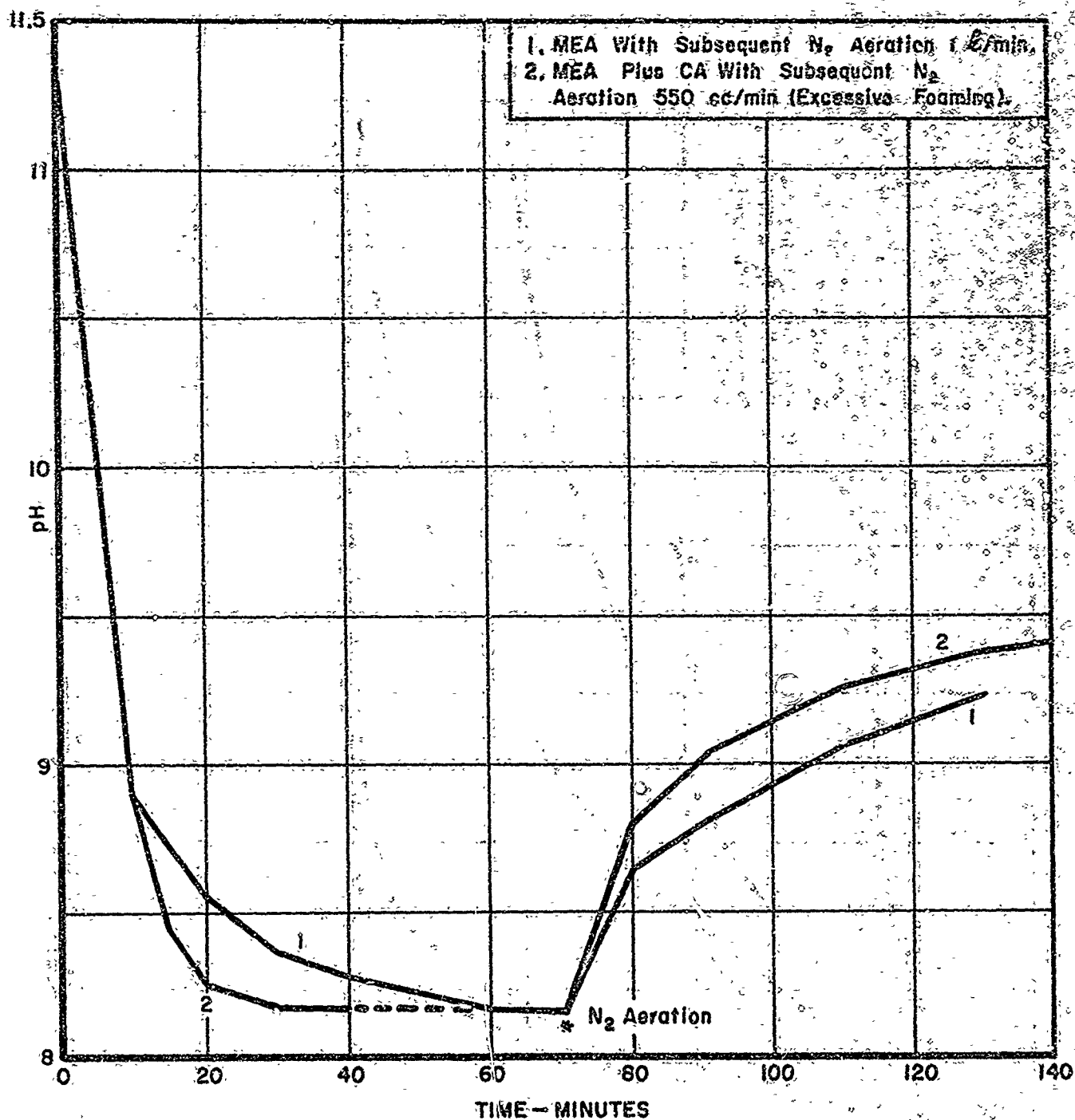


Figure 23. Changes in pH of MEA, 0.1 M, During CO_2 Absorption Run in Air Loop With 4.92% CO_2 in Air

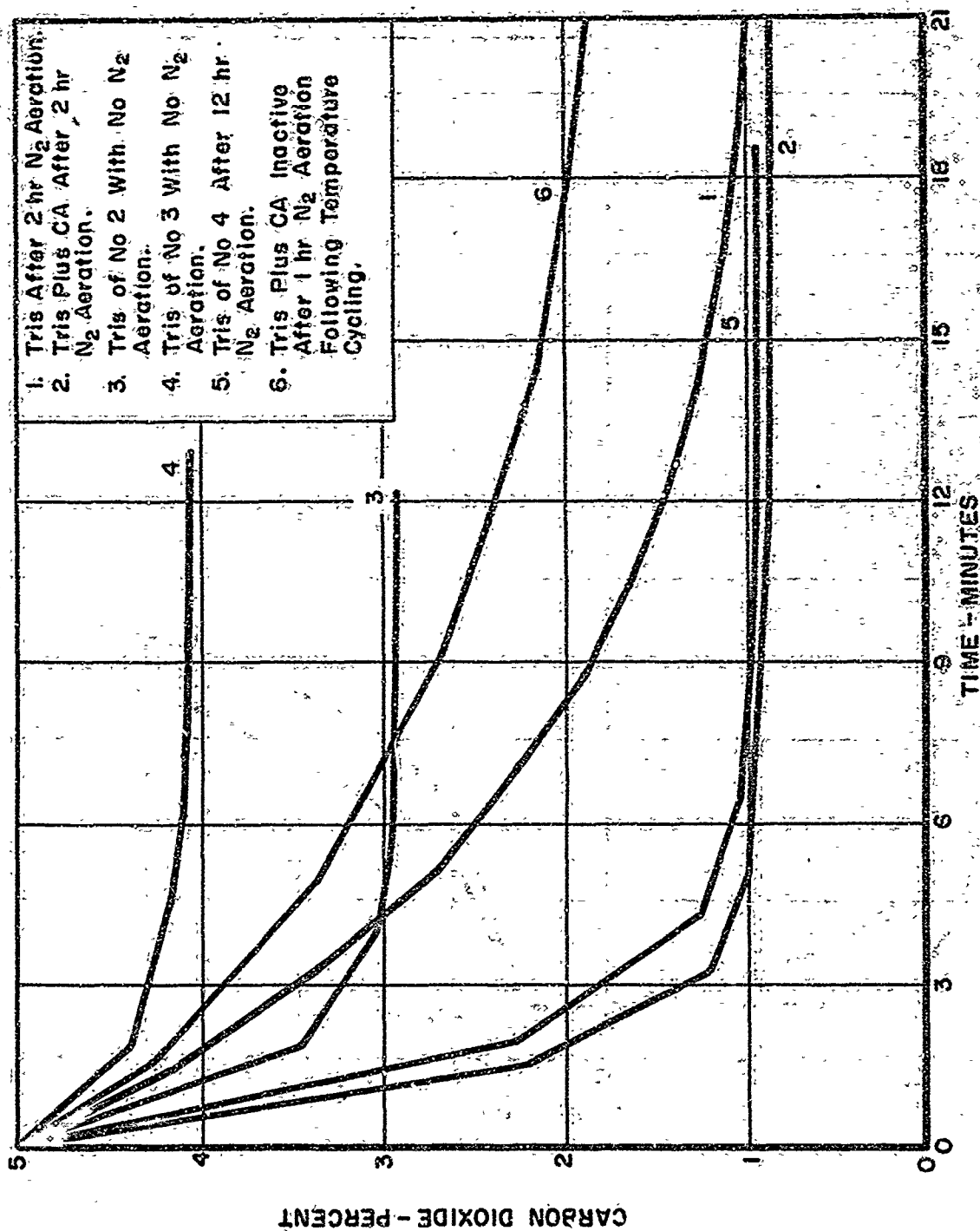


Figure 24. Regeneration of CO₂ Absorption Capacity of Tris, 0.05 M, With CA by N₂ Aeration

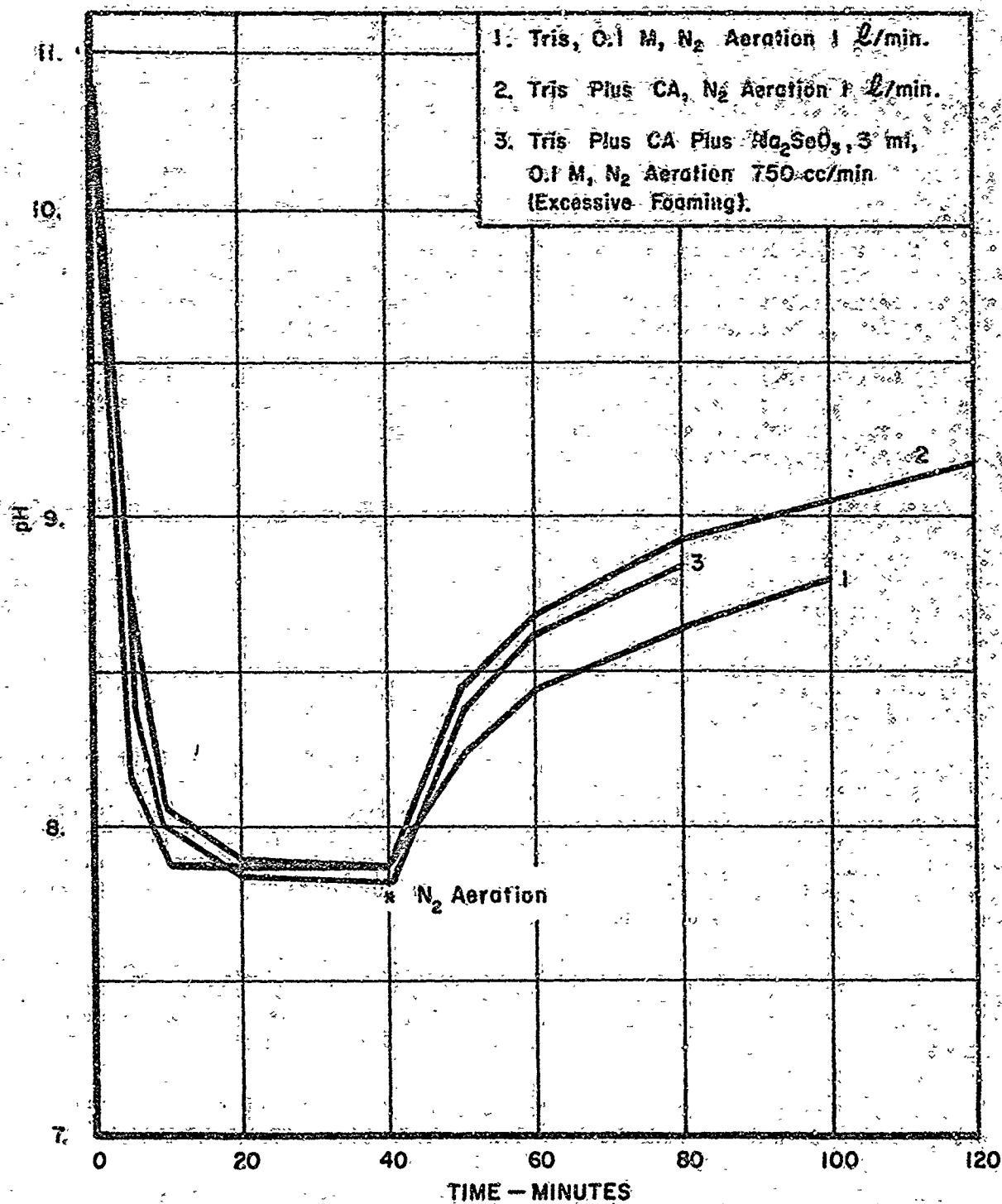


Figure 25. Effect of Sodium Selenite on pH Change of Tris Plus CA During 4.92% CO_2 in Air Aeration and Subsequent N_2 Aeration

SECTION VII

DISCUSSION OF RESULTS

The tris solution at 0.1 M revealed carbon dioxide absorption that was significantly altered by the presence of 10 mg of CA. The pH change during absorption using 4.92% in air was 1.2 to 1.4 pH units; this change was less as the initial pH was less basic. With 270 ppm CO_2 in nitrogen the pH change was small. The tris plus enzyme absorption runs were comparable to those of 0.1 N NaOH in absorption times less than 15 minutes, but not as effective as for 0.2 N NaOH. The pH of the absorber solution was directly related to the carbon dioxide concentration in the air loop. However, the carbon dioxide was never completely absorbed from the air loop with tris plus the enzyme but rather leveled off at some value less than 1/10 of the original concentration for 0.1 M tris. NaOH at 0.1 N was effective at a somewhat slower rate of absorption, but at an accelerated rate when the enzyme was present.

Absorption by tris plus the enzyme was significantly affected by the temperature of the solution. At 13°, the final concentration of carbon dioxide was lower and leveled off in a shorter time interval, as indicated in Table I. The higher temperature resulted in a higher level of residual carbon dioxide in the air loop.

A temperature change of from 13° to 32.5° raised the final carbon dioxide concentration from 0.69% to 1.67%. Then, upon cooling the absorber solution from 32.5° to 15°, the carbon dioxide content in the recirculating air loop stream dropped to 0.83%. The carbon dioxide capacity of the tris plus enzyme solution decreased 0.84% as a result of the change in temperature. The time intervals required to attain the steady temperature states in the "H" cell were comparable to the 15- to 20-minute absorption cycle as indicated in curve 1 of Figure 9. The heat exchange surface properties of the condenser, however, were definitely not optimum since the change in temperature from 15° to 32.5° required 50 minutes (curve 2 of Figure 9) and the change from 32.5° to 15° required 70 minutes.

Desorption of carbon dioxide with nitrogen aeration at 300 cc/min at 25° induced a slow pH change upwards approaching the initial pH. Ten to 12 hours aeration were needed to attain the initial pH value. A subsequent carbon dioxide absorption run revealed absorption comparable to the original desorbed solution. Carbon dioxide trapping during the nitrogen aeration with 0.1 N NaOH and subsequent titration with 0.1 N HCl revealed little carbon dioxide evolution in a 30-minute interval of nitrogen aeration. This 30-minute interval was taken as being equal to the tris carbon dioxide absorption run.

The recycling of a nitrogen stream in the air loop through the tris plus enzyme solution and then through the NaOH trapping solution at 0.1 N or at 0.2 N revealed that desorption was affected by the temperature of the absorption solution. Titration of the NaOH with 0.1 N HCl gave the values in Table II showing that higher temperatures induced the greater amount of carbon dioxide desorption.

A desorption procedure using a 32° tris plus enzyme solution with the addition of a DC potential to the H cell and with the trapping of the released carbon dioxide in NaOH should reveal significant amounts of carbon dioxide released.

Desorption procedure of tris plus CA with vacuum at 28 inches of mercury with nitrogen bubbling and the desorption gas stream passing through 0.2 N NaOH 10 ml revealed little release of carbon dioxide at 25°. The titration of the NaOH with 0.1 N HCl revealed a difference of 0.35 ml of HCl or equivalent to 0.80 cc of carbon dioxide at standard conditions. At 33° desorption of carbon dioxide with vacuum and nitrogen bubbling revealed a somewhat greater effect with 2.9 ml of 0.1 N HCl as the difference in the NaOH titration or 6.64 cc of CO_2 at standard condition.

TABLE I

CARBON DIOXIDE REMOVAL BY ABSORPTION IN TRIS IN "H" CELL

Solution	RECORDER READINGS							
	Temp (°C)	CO ₂ (%)	Initial (mm)	5 min (mm)	10 min (mm)	20 min (mm)	Differ- ence (%)	Capacity (%)
Empty H cell	25	5.0	150	133	127	126	---	---
	25	0.4	80	68	67	---	---	---
Dist H ₂ O 70 ml	25	270 ppm	135 ppm	117	111	111	---	---
	25	5.0	150	125	124	124	---	---
Tris 0.1 M	25	5.0	150	85	56	27	78	8.0
Tris 0.1 M and CA	25	5.0	150	15	11	11	91	9.3
Tris 0.1 M and CA	14	5.0	150	10	8	4	96	9.8
Tris 0.05 M	25	270 ppm	135	77	44	18	83	---
Tris 0.05 M and CA	25	270 ppm	135	44	26	20	81	---
Tris 0.05 M and CA	13	5.0	150	30	22	21	84	17.2
Tris 0.05 M and CA	25	5.0	150	37	29	29	76	15.3
Tris 0.05 M and CA	33	5.0	150	57	51	40	68	---
Tris 0.02 M	25	0.4	80	52	39	33	50	---
TM 0.02 M	25	5.0	150	80	57	46	62	---
TM 0.02 M and CA	25	5.0	150	62	50	47	62	---
TM 0.02 M and CA 10 v DC	25	5.0	150	57	46	44	64	---
TM 0.02 M and CA 7 v DC	25	0.4	80	19	16	---	76	---

TABLE II

DESORBED CARBON DIOXIDE TRAPPING IN THE BUBBLER TUBE DURING NITROGEN
RECYCLE THROUGH TRIS PLUS CARBONIC ANHYDRASE IN THE "H" CELL

No of Operation	Temp (°C)	Bubbler Tube NaOH		Titration Blank (ml)	HCl Run (ml)	Difference (ml)	CO ₂ (cc)
		(ml)	(N)				
{ NaOH in Bubbler Tube as Absorber in Sample Loop - "H" Cell Out	25	25	0.1	25.0	18.0	13.00	44.54
	25	25	0.1	25.0	12.15	12.85	---
Residual CO ₂ *	27	10	0.2	20.0	18.45	1.45	3.73
Desorbed CO ₂ -N ₂ Recycle**		25	0.2	49.8	45.20	4.60	10.53
Residual CO ₂ *	10	10	0.2	20.0	19.65	0.35	0.85
Desorbed CO ₂ -N ₂ Recycle**		10	0.2	20.0	16.65	3.35	8.16
Residual CO ₂ *	32	10	0.2	20.0	18.80	1.20	3.15
Desorbed CO ₂ -N ₂ Recycle**		10	0.2	20.0	15.00	5.00	13.13
Residual CO ₂ *	14	25	0.1	25.0	24.20	0.80	1.97
Desorbed CO ₂ -N ₂ Recycle**		25	0.1	25.0	21.60	3.40	8.40
Residual CO ₂ *	32	20	0.2	40.0	39.75	0.25	0.65
Desorbed CO ₂ -N ₂ Recycle**		20	0.2	40.0	32.20	7.80	20.48
Residual CO ₂ *	34	25	0.1	25.0	24.10	0.90	2.37
Desorbed CO ₂ -N ₂ Recycle**		25	0.1	25.0	17.60	7.40	19.49

*Enzyme-Tris Solution in "H" Cell With N₂ Recycle
Through Bubbler Tube - "H" Cell Out.

**Enzyme-Tris Solution in "H" Cell With N₂ Recycle
Through Bubbler Tube - "H" Cell In.

SECTION VIII

SIGNIFICANCE AND APPLICATIONS

In the various proposed methods for carbon dioxide control in a closed environmental control system, the decision to use a regenerative absorber or adsorber will be based primarily upon the capacity of the sorber and its regenerability. The chemical absorbers such as the alkaline metals listed in Table III, have good absorption capacity and are effective for a one-time use. They provide no regenerability, however, as to the absorption capacity or carbon dioxide recovery without prohibitive power requirements for heating temperatures to decompose the resulting carbonates. This necessarily led to the consideration of the use of the metal oxides such as magnesium oxide and silver oxide which reacted with carbon dioxide to form carbonates that decomposed at somewhat lower temperatures than those for sodium and potassium carbonates. The melting point of the magnesium carbonate, however, was 350° whereas its decomposition temperature was in the range of 449° to 549°. For silver carbonate the temperatures were 121° to 149° for decomposition, and 218° for melting, but the theoretical capacity was only 19% (0.19 lb/lb) of silver oxide. In view of this capacity, other chemical absorbers appear competitive.

The physical adsorbers, molecular sieves, have capacities of about 6 pounds of CO₂ per 100 pounds of sieve which is about 1/4 to 1/3 the capacity of silver oxide, but the sieves are subject to inactivation by preferential adsorption of water. The chemical absorbers such as the hydroxides and oxides are most effective only when water is present. Since water will be a control constituent of the recirculating and control gas stream, it is most reasonable to use a carbon dioxide control concept that is effective in the water vapor concentrations expected in the controlled atmosphere. The chemical concept thus best fits the need.

Of the regenerable chemical carbon dioxide control techniques listed in Table IV, sodium and potassium carbonates are effective but of rather limited application to closed ecological systems. The amine solutions with monoethanolamine and diethanolamine are effective but are of large plant dimensions. The monoethanolamine was subject to inactivation due to oxidation of the amine. The loss of capacity was due to stable carbonate formation of other derived compounds which required somewhat greater temperatures for desorption of carbon dioxide than those for monoethanolamine.

The use of solid amines for carbon dioxide absorption is supported by experimental data. Their use is limited, however, by their relatively low capacities (see Table V). The Gat-o-Sorb material capacity is about 1 to 2%. The resins so far evaluated are in the 1 to 2% carbon dioxide capacity. These resins are activated when water is present and are desorbed of carbon dioxide at relatively low temperatures, about 80°.

The present work with the enzyme, CA, in an amine solution has shown that tris has a proven capacity comparable to silver oxide. Graf's work (Reference 4) showed a capacity for tris in his runs with CA of 16.6% at 20° with a carbon dioxide removal of 82.5% in a 20-minute period. In the present work, the capacity for tris alone was 8.0% with a 78.2% carbon dioxide removal after a 20-minute absorption period. During a 10-minute absorption period at 25°, with the CA present in the tris, the capacity was increased to 9.3%, and 91% of the carbon dioxide was removed. The halving of the time is most significant. When a more dilute tris solution was used, a greater capacity was found, up to 15.3% with only a 76% carbon dioxide removal capacity, in a 10-minute time interval. When the absorption was run at 13° instead of at 25° as above, an increase in capacity to 17.2% was calculated, with 84% carbon dioxide removal in a 10-minute period.

TABLE III

SOLID CARBON DIOXIDE ABSORBERS

Material	Theoretical CO ₂ Capacity (lb/lb)	Carbonate Decomposition Temperature (°C)	Carbonate Melting Temperature (°C)
Lithium Oxide	1.47	---	618
Lithium Hydroxide	0.92	---	---
Sodium Oxide	0.71	699	851
Sodium Hydroxide	0.55	699	851
Potassium Oxide	0.47	727	891
Potassium Hydroxide	0.39	727	891
Magnesium Oxide	1.09	449-549	350
Magnesium Hydroxide	0.76	449-549	350
Calcium Oxide	0.79	671-838	---
Calcium Hydroxide	0.60	---	---
Silver Oxide	0.19	121-149	218

TABLE IV

LIQUID CARBON DIOXIDE ABSORBERS

	CO ₂ Solubility (cu ft/gal)		CO ₂ Net Absorption Capacity (cu ft/gal)
	25°C	75°C	
2 N Na ₂ CO ₃	2.41	1.21	1.20
4.5 N K ₂ CO ₃	5.45	2.55	2.90
4 N Triethanolamine	2.28	0.18	2.10
5 N Diethanolamine	8.55	3.00	5.55
9.5 N Monoethanolamine	15.4	12.0	3.40

TABLE V

AMINE ABSORBER CAPACITY VERSUS MOLECULAR SIEVE

Material	Type	Absorption Capacity	Percent Regeneration
IR 45 Rohm & Haas	Weak Base Resin	5.4 mg CO ₂ /cc	42
Permutit A	Medium Base	5.6 mg CO ₂ /cc	6
Nalcite SAR	Strong Base	26.9 mg CO ₂ /cc	6
Epon 562 and Di-ethylene triamine	Excess Amine	20.6 mg CO ₂ /cc	100
Resin Slurry Polyethyleneimine	----	20.6 mg CO ₂ /g	----
Gat-o-Sorb	----	1-2% CO ₂	----
Tris Plus CA	----	17.2% CO ₂	----
Molecular Sieve	4A	6.7 mg CO ₂ /g	----
	5A	6.3 mg CO ₂ /g	----
	13X	5.0 mg CO ₂ /g	----

The enzyme catalyzed carbon dioxide adsorption by amines has a possible application to solid carbon dioxide absorbers which are chemically active in the presence of water vapor in the controlled gas stream. A significant reduction was indicated in the time of absorption for the amines. The absorber capacity remained high and the reaction with carbon dioxide indicated a steep absorption front. The regenerability of an enzyme catalyzed amine absorber, however, requires additional study as to its limitations. The enzyme activity is limited to temperatures below 40° and thus heat regeneration is not indicated. The vacuum desorption was apparently not too effective under the conditions that existed during this effort. The application of electrical potentials to the sorbing medium should be investigated further since a positive effect upon desorption was indicated.

SECTION IX

SUMMARY

The in-house investigations described in this report evaluated the effectiveness of CA in catalyzing a carbon dioxide absorption and desorption process in tris solution. The CO_2 removal curves provided the data on capacity and effectiveness and the basis for comparison with standard absorbers.

Tris enzymic solutions effectively removed 70 to 80% of the carbon dioxide in a gas sample in short time intervals of 10 minutes. Temperatures near room ambient enhanced the capacity and the removal percentages. Temperatures above room ambient favored desorption of carbon dioxide and limited enzyme activity when above 40°.

Further study is required on the specific effects of oxygen and amine interactions as these affect the carbon dioxide hydration catalyzed by the enzyme.

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13. ABSTRACT One concept of carbon dioxide control in aerospace vehicle atmosphere regeneration and control requires an efficient gas absorber which is effective in a moist gas stream. A tris (tri(hydroxymethyl)aminomethane) solution containing the enzyme, carbonic anhydrase (CA), was studied as to carbon dioxide absorption and desorption. The carbon dioxide content and the pH changes were monitored during the recycling of a gas mixture through the absorber solution. Desorption was accomplished by nitrogen aeration. The application of DC potentials to the absorber solution indicated an acceleration of carbon dioxide desorption. Vacuum desorption of carbon dioxide without nitrogen bubbling was not effective. Nitrogen aeration at 33°C was more effective than at room temperature or at 13°C. This pH of the enzyme-tris solution varied inversely with the carbon dioxide content. The tris solution was a more effective carbon dioxide absorber than 0.1 N NaOH when the enzyme was present. A long time stability of approximately five weeks for a 70-ml aliquot of tris at 0.1 N with 10 mg of CA was indicated by the repeated absorption and desorption runs made in the regeneration studies. The application of a buffered enzyme solution to carbon dioxide control is supported by a rapid removal rate from a recycling air stream and a regeneration capability. This concept of carbon dioxide control requires additional research for the evaluation of techniques to accelerate the carbon dioxide desorption process. (This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Flight Dynamics Laboratory (FDDE), Wright-Patterson Air Force Base, Ohio 45433.)		

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